DETERMINATION IN AQUEOUS MEDIA OF INTERELEMENT CORRECTION COEFFICIENTS TO BE USED IN THE ANALYSIS OF ALUMINUM ALLOYS BY XRF AND DETERMINATION OF THE ABSORPTIVE EFFECTS OF MYLAR FILM SPECIMEN CELL COVERINGS

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A Thesis

in

The Department of Chemistry

Presented in Partial Fulfillment of the Requirements for
the Degree of Master of Science at
Concordia University
Montreal, Quebec, Canada

April, 1975

ABSTRACT

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DETERMINATION IN AQUEOUS MEDIA OF INTERELEMENT CORRECTION COEFFICIENTS TO BE USED IN THE ANALYSIS OF ALUMINUM ALLOYS BY XRF AND DETERMINATION OF THE ABSORPTIVE EFFECTS OF MYLAR FILM SPECIMEN CELL COVERINGS

This study provides a background for the use of x-ray fluorescence spectrometry (XRF) in a projected investigation, the analysis of commercial aluminum alloys. Aqueous solution systems are employed, at levels of component concentrations such that the absorption and/or enhancement effects are appreciable, in order to obtain resonably accurate estimations of the α-correction coefficients.

The first portion of the investigation involved the determination of the absorptive effects of mylar film specimen cell coverings. The second portion involved the determination of the Lachance-Traill α-correction coefficients associated with certain elements of interest relative to the analysis of aluminum alloy compositions.

ACKNOWLEDGEMENTS.

The author wishes to express his sincere appreciation to Professor J.G. Dick for his valuable guidance throughout the investigation.

The author thanks Dr. A.D. Nguyen for the many helpful discussions.

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1. INTRODUCTION

The quantitative determination of elements by x-ray fluorescence (XRF) presents certain problems, the main difficulty is involving the specimen itself. The validity of the analytical determination depends on the physical structure and chemical composition of the specimen. The problem of physical structure would be solved if the specimen was completely homogenous, with a particle size or surface roughness less than the critical value dictated by the analyte of longest emission wavelength.[1,2,3] This situation is not easily achieved for solid specimen. The use of solution specimens tends to eliminate heterogeneity, surface roughness and particle size problems.

A problem of chemical composition is generally referred to as the matrix effect or interelement effect. This results in a nonlinear relationship between emitted radiation intensity and concentration of the emitting element.

Consider a multi-component system (A, B, C, ...). Let I_A be the intensity of a characteristic line from element A in this multi-component system, and I_A^o be the intensity of that line from the pure element A. Then if C_A is the weight fraction of element A in this system, the ratio of

intensities for a given line from a sample and a pure element should be directly proportional to the weight fraction of the element in the specimen being analyzed.

$$I_A / I_A^{\circ} = C_A \quad \text{or} \quad I_A = C_A I_A^{\circ}$$

However, the deviations occur which may either increase or decrease the intensity (I_A) from the value calculated from the above equation. Such deviations are generally due to the absorption and/or enhancement effects of each matrix element on any other matrix element.

A number of authors[4,5,6,7,8], have carried out the theoretical studies of the absorption-enhancement effect. These usually involve the derivation of the primary fluorescent intensity due to excitation by the incident beam, and the secondary fluorescent intensity due to excitation by the characteristic radiation of the matrix element. For the expected x-ray intensity I_A of an element A, in a thick specimen S excited by a polychromatic incident radiation. The primary fluorescent intensity at radiation α for element A can be written as shown in equation 1. The secondary fluorescent intensity at radiation α for element A, due to excitation by the characteristic radiation β for element B, can be written as shown in equation 2. If the enhancement

$$I_A(1) = \frac{q}{\sin\varphi} E_A C_A \int_{\lambda_o}^{\lambda_{edge}} \frac{\mu_A(\lambda) I_o(\lambda)}{C_A\bar{\mu}_A(\alpha) + C_B\bar{\mu}_B(\alpha) + C_C\bar{\mu}_C(\alpha) + \ldots} d\lambda \qquad (1)$$

$$I_A(2) = \frac{q}{\sin\varphi} E_A \omega_A \mu_A(\beta) \int_{\lambda_o}^{\lambda_{edge}} \frac{E_B C_B \mu_B(\lambda) I_o(\lambda) L}{\left[\mu(\lambda)/\sin\varphi + \mu(\alpha)/\sin\psi\right]_B} d\lambda \qquad (2)$$

where:-

$I_A(1)$ = the primary fluorescent intensity, radiation α for A

q = the fraction of fluorescent intensity passing through the collimator towards the crystal

E_A = a factor dependent upon the atomic number of A, with the value:-

$$E_A = \frac{S_K - 1}{S_K} W_K p_\alpha$$

where:-

S_K = the absorption jump ratio for K radiation

W_K = the fluorescent yield for the K series

p_α = the fraction of the fluorescent yield related to α radiation

$I_o(\lambda)$ = the incident intensity at wavelength λ

$C_A, C_B,$ = the weight fraction of the elements A, B, ...

$I_A(2)$ = the secondary fluorescent intensity, radiation α for A

φ = the incident angle

ψ = the emergent angle

λ_o = the minimum wavelength of the primary spectrum

λ_{edge} = the wavelength at the absorption edge for A

$\bar{\mu}_A(\ ) = \left[\frac{\mu(\lambda)}{\sin\varphi} + \frac{\mu(\alpha')}{\sin\psi}\right]_A$ = the average absorption coefficient of A at the incident radiation and the fluorescent radiation

$$L = \left[\frac{\ln\left(1 + \frac{\mu(\phi)}{\mu(\beta)\sin\varphi}\right)}{\mu(\alpha)/\sin\varphi} + \frac{\ln\left(1 + \frac{\mu(\alpha)}{\mu(\beta)\sin\psi}\right)}{\mu(\lambda)/\sin\psi}\right]$$

effect can be considered as a negative absorption effect, the intensity equation may be dramatically simplified by eliminative of the secondary fluorescent intensity equation. This concept was originated by Noakes[9] in 1954, and was later applied by Birks[10] and Claisse and Quintin[11].

If one now considers the polychromatic primary radiation to behave exactly like a single monochromatic wavelength λ_{eff}, the fluorescent intensity equation may be rewritten as shown in Equation (3).

$$I_A = \frac{q}{\sin\varphi} E_A C_A \frac{\mu_A(\lambda_{eff}) I_o(\lambda_{eff}) \lambda_{eff} \ldots}{C_A \bar{\mu}_A(\alpha) + C_B \bar{\mu}_B(\alpha) + \ldots\ldots} \qquad (3)$$

Where:

$$\bar{\mu}_A(\alpha) = \left[\frac{\mu(\lambda_{eff})}{\sin\varphi} + \frac{\mu(\alpha)}{\sin\psi}\right]_A$$

In the expression above, in the case of enhancement,

μ' is a hypothetical absorption coefficient.

If the intensity ratio (R) is used, the parameter constants, with the exception of the mass absorption coefficients, are eliminated, and Equation (3) is reduced to Equation (4):-

$$R_A = \frac{I_A}{I_A^o} = \frac{\bar{\mu}_{oA} C_A}{C_A \bar{\mu}_A + C_B \bar{\mu}_B + C_C \bar{\mu}_C + \ldots} \qquad (4)$$

where I_A^o is the fluorescent radiation intensity for pure element A.

Beattie and Brissey[12] were among the first to propose a series of relationships which can be developed on theoretical grounds. While their approach is theoretically correct, in practice it shows rather large relative error.

In 1966, Lachance and Traill,[13] starting from the same fundamental equations, developed a series of expressions which are essentially similar to those of Beattie and Brissey, but which are presented in a different mathematical form.

In Equation (4), if C_A in the denominator is replaced by $(1 - C_B - C_C - \ldots)$, and terms rearranged, one obtains Equation (5):-

$$R_A^o = \frac{I_A}{I_A^o} = \frac{C_A}{1 + \alpha_B\left(\frac{\bar{\mu}_B - \bar{\mu}_A}{\bar{\mu}_A}\right) + C_C\left(\frac{\bar{\mu}_C - \bar{\mu}_A}{\bar{\mu}_A}\right) \pm \ldots}$$

$$= \frac{C_A}{1 + \alpha_{AB}C_B + \alpha_{AC}C_C + \ldots} \qquad (5)$$

where:-

$$\alpha_{AB} = \frac{\bar{\mu}_B - \bar{\mu}_A}{\bar{\mu}_A}$$

and represents the effect of the element B on element A.

Every coefficient can be evaluated from every one series of several standard binary sample, which contain A,B or A,C or A,D ... etc, using a relationship derived directly from the basic Lachance and Traill Equation (5). This is given as

$$\alpha_{AB} = \frac{I_{A(1)}C_{A(2)} - I_{A(2)}C_{A(1)}}{I_{A(2)}C_{A(1)}C_{B(2)} - I_{A(1)}C_{A(2)}C_{B(1)}} \qquad (6)$$

the subscripts 1 and 2 indicate the standard sample 1 and 2.

The problems encountered in the XRF determination of light elements can be summarized as follow:-

(1) a reduction in excitation efficiency

(2) an increase in absorption of fluorescent or emitted x-ray throughout the optical path of the spectrometer from specimen to detector.

(3) a resulting decrease in signal and in signal to noise ratio, and thus in sensitivity.

(4) the specimen preparation is more critical.

(5) a lower order of available data concerning the x-ray interaction (matrix effect).

Problems (1) and (2) are instrumental, and much has been accomplished towards their solution. This has, to a degree, minimized Problem (3). Problems (4) and (5) are highly dependent upon the analyses attempted, and generalization is difficult. However, in an analysis using a liquid sample, because of the leveling nature of the solvent, the technique helps to minimize and clarity the matrix effects. The lower absorption of the solvent matrix permits dilution factors which would be prohibitive in powder samples because of intensity losses. In addition, liquid samples are readily adaptable to the use of the addition technique of analysis. The aqueous solution technique has been applied by several investigators, among whom are Waterbury and Hakkila,[14] Zimmerman and Ingles,[15] Kang, Keel and Solomon[16] and Dwiggins.[17] In such instances

the effects of absorption and enhancement were reduced to levels where they could be ignored, this being accomplished by the use of highly dilute solutions of the analytes of interest. With solids concentrations totaling approximately 10 percent by weight, absorption and enhancement effects can not be ignored and the use of correction coefficients for such effects is mandatory. The higher emission intensities permit greatly improved accuracy and precision. Work in this area has been carried out by Dick and Nguyen,[18] and the report indicates very good accuracy and precision with respect to the determination of a wide range of components in extensive ranges of concentration.

In the determination of light elements by XRF analysis, using the liquid solution technique, the absorption effect due to the mylar film cell covering, especially at the longer wavelength x-ray must be considered. In certain instances more than 60 percent of the emitted radiation can be absorbed by the mylar film. In such cases, the intensity loss decreases the sensitivity of determination. Beard and Proctor[19] have tried the trace analysis of elements sulfur, silicon and aluminum in the solution technique by XRF analysis. They used either mylar covered or uncovered specimens and compared both methods. The result shown in Table 1.1. were obtained. The limit of detectability is shown in the last column of this table. The

TABLE 1.1

Comparison of Methods (Mylar Covered and Uncovered)

Element	Concentration (ppm)	Method	Peak Intensity (c.p.s.)	Background Intensity (c.p.s.)	Net Peak Intensity (c.p.s.)	Limit (ppm)
S	150	Uncovered	201	84	117	4
S	150	Mylar Covered	176	89	87	5
Si	146	Uncovered	10	2	8	7
Si	146	Mylar Covered	6	2	4	14
Al	130	Uncovered	17	3	14	4
Al	130	Mylar Covered	11	3	8	8

* Intensity measurement based on 100 second counting time

original tabled values have been modified to resonable significant figure expression.

Actually, the mylar effect can be previously determined, and depends on the wavelength of the impinging x-ray and the thickness of the mylar film. The simple expression for the relationship between the intensity uncovered I^o and the intensity mylar covered I can be shown as:-

$$I(\lambda) = I^o(\lambda)\, e^{-kx} \qquad (7)$$

where:-

k = constant dependent on film composition and wavelength of incident beam.

x = thickness of mylar film

λ = wavelength of the characteric line of element

Since the K radiation has a characteric wavelength for each element, the k constant can be easily determined for a given thickness of mylar film. Therfore, the transmittance of mylar to secondary x-ray may be calculated, and the uncovered intensity given by:-

$$I^o = \frac{I}{e^{-kx}} \qquad (8)$$

2. EXPERIMENTAL

2.0 General

The present studies were intended to investigate:-

(1) the mylar absorption for the x-ray K_α radiation.

(2) the absorption-enhancement effect of the aqueous matrix M and of other elements which might be contain in aqueous solutions of commercial aluminum alloys. The Lachance-Traill α-correction coefficients for the effect of aqueous matrix and associated other elements were determined.

2.1 Sample Preparation

Solid standard samples supplied by Somar Ltd., were used in the mylar absorption investigation. They were also used to set up the instrumental parameters for XRF analyses.

A series of solutions for each element of interest were prepared. These solutions, in each case, showed considerable variation in the concentration range, generally from 0.005 to 0.1 weight fraction. Each series of solutions was prepared, from stock solutions, by the dilution method. The final weight of each prepared solution specimen was generally 50 g, and the dilution water was boiled previously due to prevent the formation of gas bubbles during the XRF analysis.

The stock solutions, with concentrations of 0.05 g, 0.1 g, or 0.2 g per ml, were prepared for each element by dissolving the appropriate material in nitric acid. The chloride stock solution was prepared from concentrated hydrochloric acid by dilution, and the chloride concentration was accurately determined by potentiometric titration using standard silver nitrate solution and a silver-silver/silver chloride combination electrode.

2.2 Instrumentation

In this investigation, a Picker Nuclear Spectrodiffractometer, a 2-tube ultrastable generator and a radiation analyzer were used. The fluorescence spectrometer had 45° incident and emergent angles.

2.2.1 X-ray tubes

The choice of x-ray tube target for optimum excitation of a particular type of specimen depends on several factors which must be judged relative to each other.

(1) Only a few elements have suitable thermal and mechanical properties for x-ray tube targets. Tungsten is most common target material, since it has a very high melting point and a resonable thermal conductivity for cooling purposes.

In addition, it has a high atomic number, and yields an intense spectrum. Tungsten is not used exclusively as a target material. The use of the characteristic lines of other targets materials, such as platinum, molybdenum, silver, copper, iron and chromium, in order to enhance the excitation of particular elements in the specimen is common. For instance, a silver target is ideal for exciting molybdenum, chromium for exciting titanium and aluminium, etc.

(2) Tube window thickness is important, especially for the excitation of the low atomic number elements. However, thin-window tubes are more fragile and can provide for service life problems.

From the considerations of (1) and (2) of the foregoing, perhaps the best minimum complement of tubes would be a standard tungsten target tube and a thin-window chromium target tube, since this would give resonable coverage for most analytical situations. In the present studies, a chromium target x-ray tube with 0.25 mm beryllium window thickness, operating at 50 kV and 36 mA, was used in the MgK_α, AlK_α, SiK_α, PK_α, SK_α and ClK_α intensity measuring process. A tungsten tube with 1.5 mm beryllium window thickness, operating at 50 kV and 20 mA, was used in the intensity measurements associated with the characteristic radiations (K_α) of the other elements such

as calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper and zinc etc.

2.2.2 Dispersive devices

The flat, reflection-crystal optical system is probably the most common of all the XRF techniques, and the crystal interplanar spacing d determines the angle θ at which the nth order of wavelength λ will be diffracted according to the Bragg equation

$$n\lambda = 2d \sin \theta \qquad (9)$$

Table 2.1. lists common crystals used in x-ray spectrometers and the d spacings and 2θ values for several analyzing crystals. In practice one should generally use the smallest-spacing crystal possible consistent with the maximum wavelength[20] to be measured. In this case, ADP is the efficient crystal for the diffraction of MgK_α, PET for AlK_α throuth ClK_α, and LiF for CaK_α through ZnK_α.

2.2.3 Collimation requirements of the spectrometer

The selection of the optimum secondary collimator for a certain application must be made with due consideration given

TABLE 2.1

USEFUL RANGES AND 2θ VALUES FOR SEVERAL ANALYZING CRYSTALS

		d-spacing			
		4.03	8.74	8.81	10.65
Element	K-line (Å)	LiF	PET	EDDT	ADP
Mg	9.8)				136.5
Al	8.34		145.1	142.0	103.1
Si	7.13		109.3	108.0	84.0
P	6.15		89.4	88.6	70.6
S	5.37		75.8	75.1	60.6
Cl	4.73		65.5	54.9	52.7
K	3.73	136.6	50.5		
Ca	3.36	113.1	45.1		
Ti	2.75	86.1			
V	2.51	76.9			
Cr	2.2)	69.4			
Mn	2.10	62.9			
Fe	1.94	57.5			
Co	1.7)	52.8			
Ni	1.66	48.6			
Cu	1.54	45.0			
Zn	1.44	41.8			

to the dispersion of the analysing crystal employed.[21] A choice is frequently available between, on the one hand, a fine collimator and a crystal of poor dispersion but high reflectivity and on the other hand, a coarse collimator and a crystal of high dispersion but poor reflectivity. Therefore, a coarse collimator can be used in the intensity (K_α) measurements for the elements from magnesium through vanadium, and a fine collimator for the elements from chromium upwards.

2.2 Intensity detection

The basic problem of x-ray detection is that of covertting the x-ray into a form of energy which can be measured and integrated over a finite period of time. There are two types of detector which are used in this investigation.

(1) The proportional flow counter (PF) with P10 gas (argon 90%/methane 10%) flow, has a useful range of from 0.7 to 10 Å wavelength. This detector was used in K_α intensity measurements for the elements magnesium through vanadium.

(2) The scintillation counter, useful wavelength is from 0.1 Å to 3 Å. This detector was used in the K_α intensity measuring process for the elements chromium upwards.

In the opration of detectors the relatively slow dissipation of the positive ion sheath has a very significant effect upon the functioning of the counter in that, as long as the

ions are in the immediate vicinity of the anode, the field is reduced thus preventing futher avalanches. This gives rise to the so called dead-time of the counter, and a useful expression for the true counting rate first proposed by Ruark and Brammer[22]

$$I_t = \frac{I_m}{1 - I_m t} \qquad (10)$$

where:-

I_t = true count rate
I_m = measured count rate
t = dead-time of the counter

In practice, for I_m 30,000 c.p.s., a dead-time correction was made.

2.2.5 Sample container

The solution subjected to XRF analysis were contained in Spex liquid cells, 1 inch in diameter and 1.25 inches in depth. Such cells hold approximately 10 ml of solution. The cell was covered with a mylar film 0.0025 inches in thickness. Considerable effort and care was taken to avoid the inclusion of air bubbles, and to maintain a flat exposed surface.

2.3 Absorptive Effect of Mylar Film

The liquid phase sample is particularly convenient since it offer a very simple means for the preparation of standards. The effects of sample physical structure can be successfully overcome by taking the sample into liquid solution, but problems may also arise out of variations in the thickness and/or composition of the specimen covering film. The most commonly used type of film is mylar film, since its ash content is low (usually less than 0.005 weight percent) and any impurities are relatively evenly distributed. In addition, since its average atomic number is low, the mass absorption coefficient is relatively low. Nevertheless it will be seen that the intensities of longer wavelength radiation is considerably reduced.

If the composition of mylar film is homogeneous, then the fraction dI/I absorbed of a beam of x-rays of intensity I, as it passes through a thin mylar film, is proportional to the thickness dx of the film. Thus we have:-

$$dI/I = -k\,dx \qquad (11)$$

Here k is the factor of proportionality, with the negative sign indicating a decrease in intensity. In addition, the factor k is dependent on the film material and x-ray wavelength. Rewriting and integrating the Equation (11) we have:-

$$\ln I_x - \ln I_o = -kx \qquad (12)$$

therefore:-

$$I_o = \frac{I_x}{e^{-kx}} \qquad (13)$$

It is clear from the latter expression that I_x is the intensity with mylar covered in thickness x, and I_o represents the intensity of x-ray when x is zero, at which the intensity is not decreased by mylar film.

2.3.1 Determination of the k value for mylar film effect

Using different thicknesses for the mylar film covering, the $K\alpha$ radiation for elements of atomic number 12 to 30 were measured. It is apparent that the thicker the mylar film used, the lower the intensity that is measured. In addition, the lower the atomic number of the emitting element, the greater the reduction in intensity.

From the Equation (12) k may be written as:-

$$k = \frac{\ln I_o - \ln I_x}{x} \qquad (14)$$

or

$$k = \frac{\ln I_2 - \ln I_1}{x_1 - x_2} \qquad (15)$$

where:-

I_o = the intensity without mylar covering

x = the thickness of mylar film

subscripts 1 and 2 = samples with different thicknesses of mylar films x_1 and x_2.

Each k value corresponding to the thickness of mylar film can be calculated by Equation (14) or (15), and the average k value approximales the constant for the wavelength or element involved.

For example, in the determination of the k value for the mylar film effect for AlK_α radiation. Table 2.2 shows the result. The value of $I_o(Al)$, representing the uncovered specimen, can be calculated by Equation (13). If 25×10^{-5} inches thick mylar film was used for covering, $I_o(Al)$ is given as:-

$$I_o(Al) = \frac{I_{meas.}(Al)}{e^{-0.05481 \times 25}} \qquad (16)$$

In a similar manner, for a liquid sample with 0.035 weight fraction of aluminium, AlK_α radiation intensity was determined and the k value was calculated, as 0.05460 ± 0.00080, by Equation (15). Using the same approach, $I_o(Al=0.035)$ may be calculated from I_x using the Equation (13).

Figure 2.1 and Figure 2.2 show the intensities for AlK_α versus the thickness of mylar covered for a pure solid

TABLE 2.2

THE k VALUES FOR THE DIFFERENT THICK MYLAR FILMS EFFECT FOR AlK_α RADIATION

Thickness (10^{-5} inches)	0	15	25	30	45	50	75
Intensity (c.p.s.)	93428	41183	23235	18044	8038	6027	1575
k	---	0.05461	0.05566	0.05481	0.05451	0.05482	0.05444

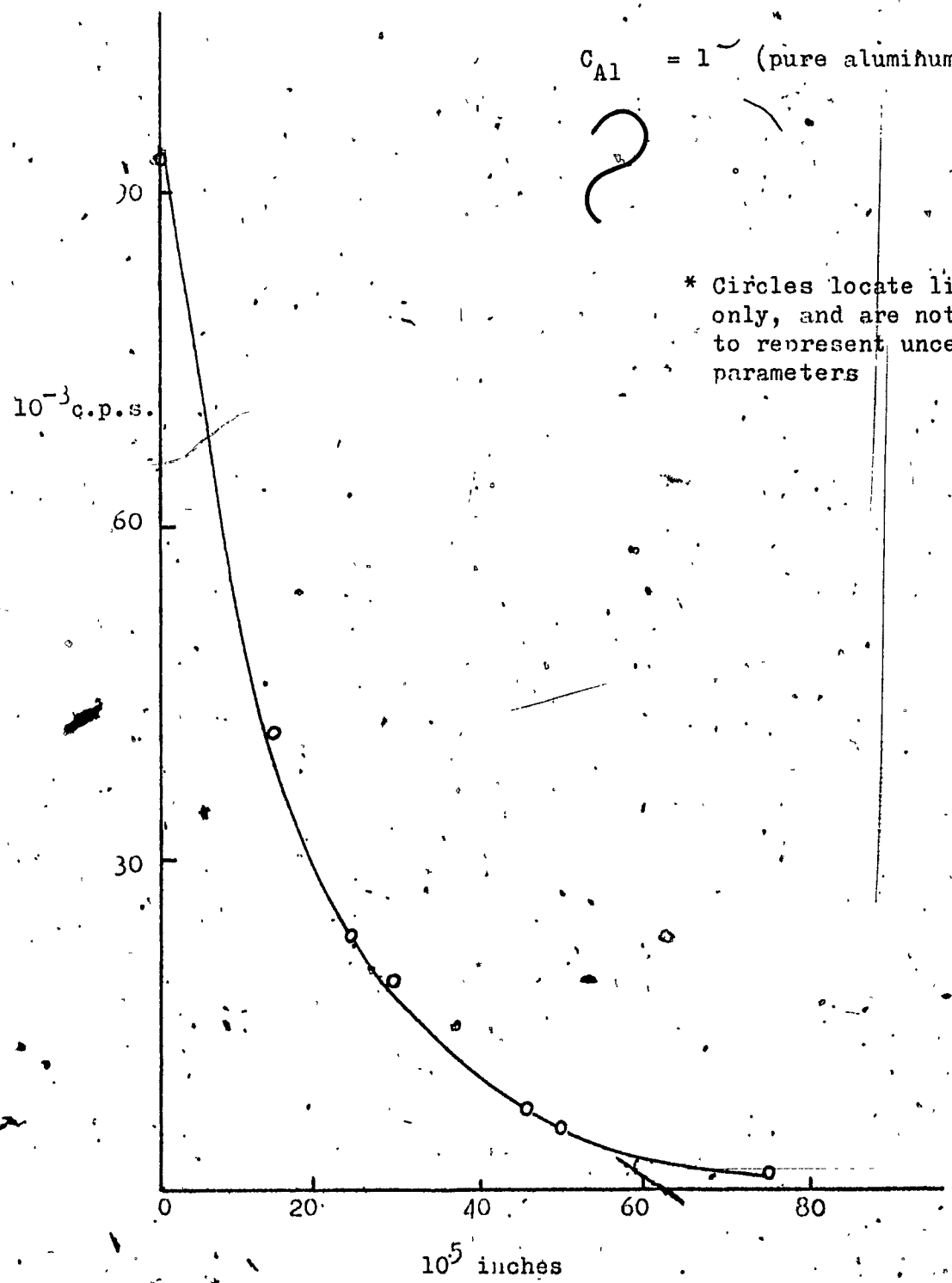
average k = 0.0548[1]

std. dev. = $\pm$ 0.0005[0]

FIGURE 4.1

$I_{AlK\alpha}$ VERSUS THICKNESSES OF MYLAR COVERED

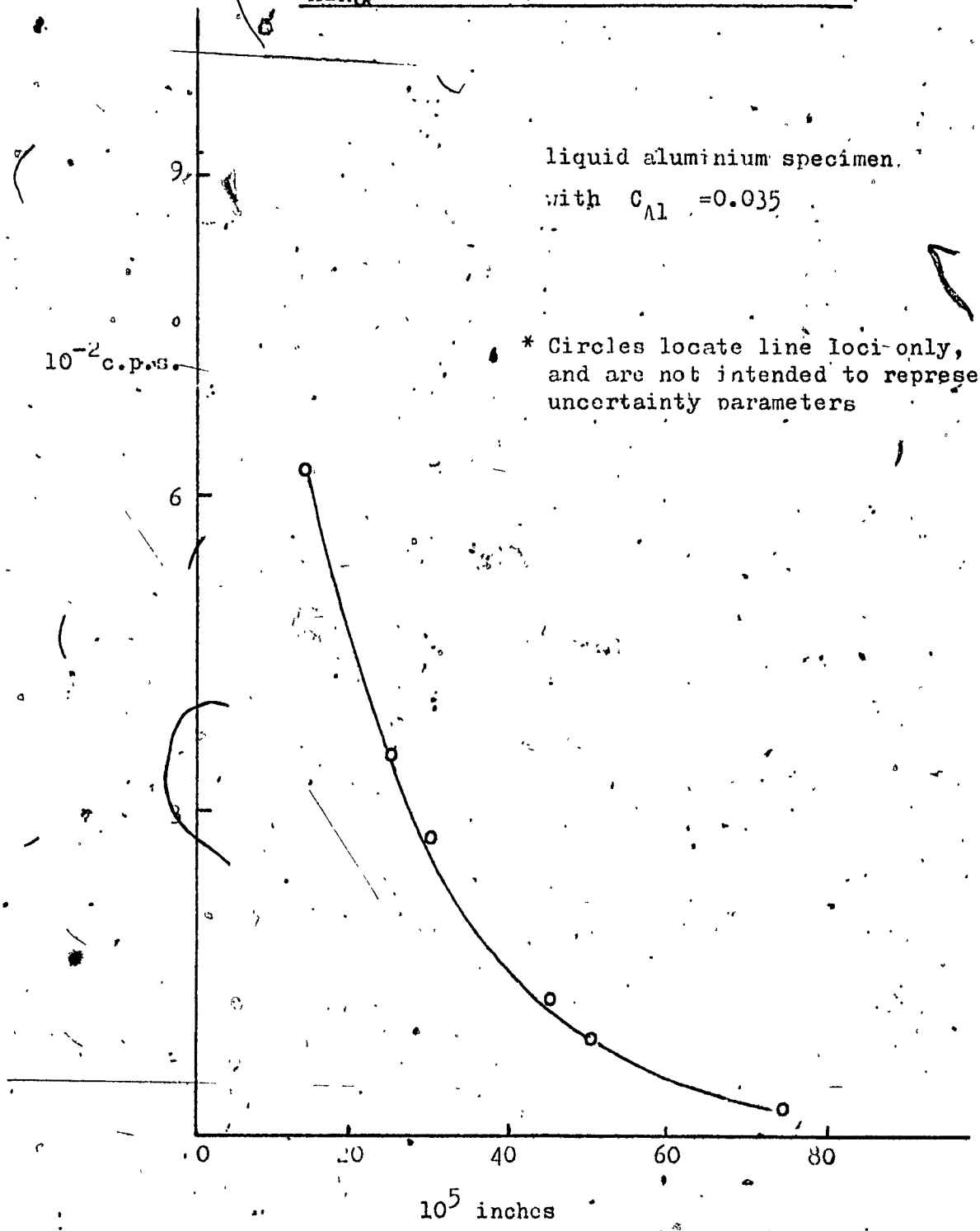
C_{Al} = 1 (pure aluminum).



* Circles locate line loci only, and are not intended to represent uncertainty parameters

FIGURE 2.2

$I_{AlK\alpha}$ VERSUS THICKNESSES OF MYLAR COVERED



aluminium sample and for a liquid solution sample with 0.035 weight fraction of aluminium respectively.

A number of element were carried through the same approach, and the associated k values were determined. The raw data may be found in Section 4.1.. The k values for each element are shown in the Table. 2.3.

Figure 2.3. shows the plotted k values versus atomic number and characteristic wavelength of interest.

2.4 α-Correction Coefficient Determination

The aqueous matrix in this work consisted most frequently of water and nitric acid. It has been recognized that the variation of nitric acid concentration does not influence significantly the fluorescent intensity of the elements.[23] Therefore, the water-nitric acid matrix is identical from one sample to another and can be designated as M.

The correction coefficient for the effect of M or any another element on an analyte element can be evaluated from two standard solutions using a relationship derived directly from the basic Lachance-Traill equation, and which was given previously as Equation (6). Several standard solutions are

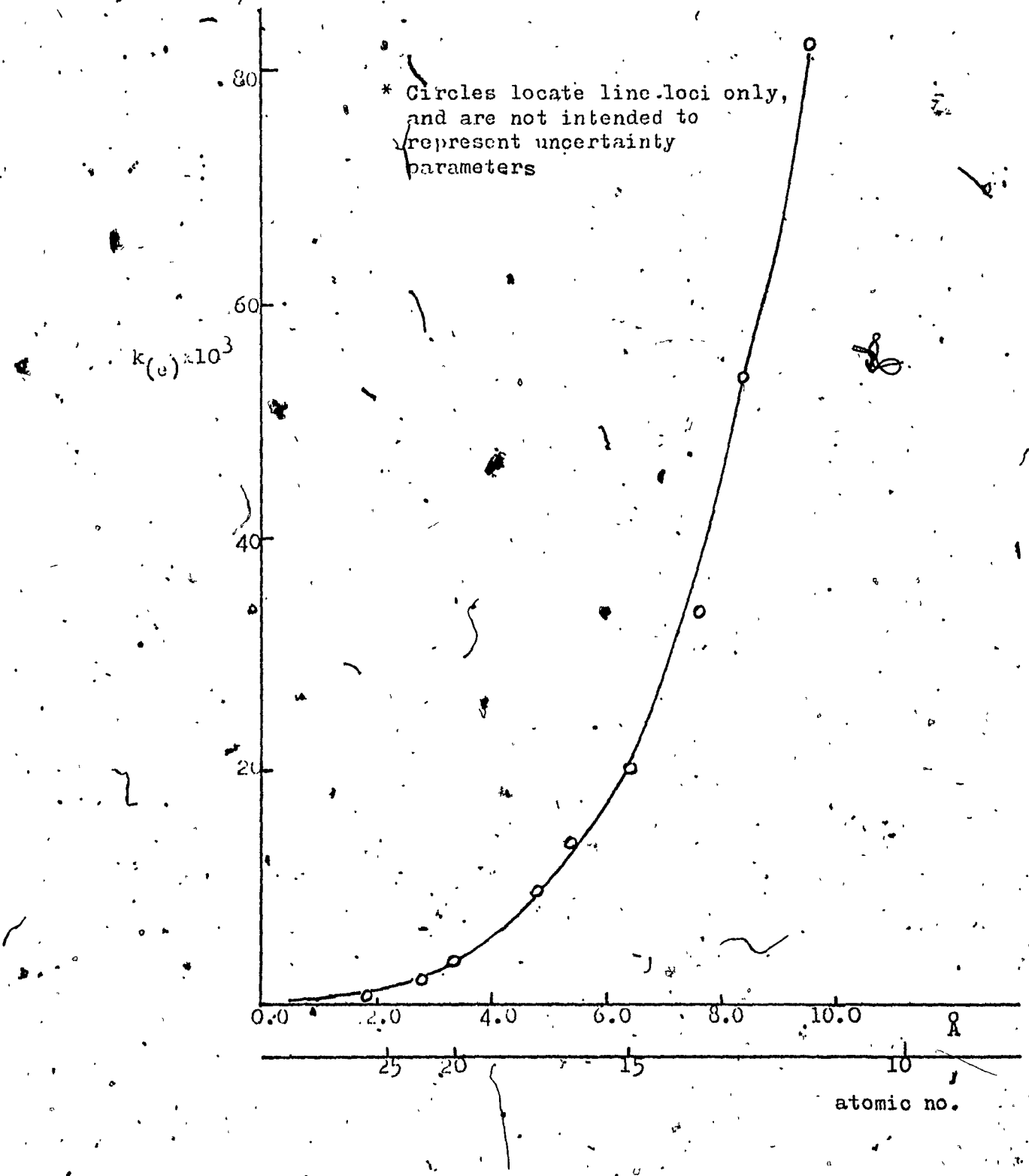
TABLE 2.3

k VALUE DETERMINATIONS FOR MYLAR COVERINGS ABSORPTION IN XRF ANALYSIS

Element	$k_{(10)}$	$k_{(e)}$	$1/e^{25k}$	Transmittance	Wavelength (Kα)
Mg	0.1002	0.06262	7.8894	12.68	9.889
Al	0.1262	0.05481	3.9363	25.40	8.339
Si	0.07954	0.03455	2.3717	42.16	7.126
P	0.04743	0.02060	1.6736	59.75	6.155
S	0.03321	0.01442	1.4341	69.73	5.373
Cl	0.02198	0.009545	1.2635	78.77	4.729
Ca	0.009193	0.003992	1.1050	90.50	3.360
Ti	0.004809	0.002088	1.0536	94.91	2.750
V	0.004789	0.002080	1.0534	94.93	2.505
Cr	0.003001	0.001303	1.0331	96.79	2.291
Mn	0.002034	0.0008821	1.0223	97.82	2.103
Fe	0.001697	0.0007371	1.0860	98.17	1.937
Co	0.001313	0.0005702	1.0144	98.58	1.791
Ni	0.0009167	0.0003981	1.0100	99.01	1.659
Cu	0.0006912	0.0003002	1.0075	99.26	1.542
Zn	0.0004925	0.0002139	1.0054	99.47	1.437

FIGURE 2.3

k VERSUS ATOMIC NUMBER AND WAVELENGTH OF Kα LINE OF ELEMENTS*



used in this connection.

2.4.1 Determination of net intensity

Theoretically the net intensity is equal to the peak intensity of a wavelength from the element in the matrix, minus the true background intensity. In practice an equivalent background position well away from the analytical line is chosen. This is shown in Figure 2.4.

Several problems may arise in the determination of the net intensity, such as:-

(1) a reduction in intensity due to the absorptive effect of the mylar covering.

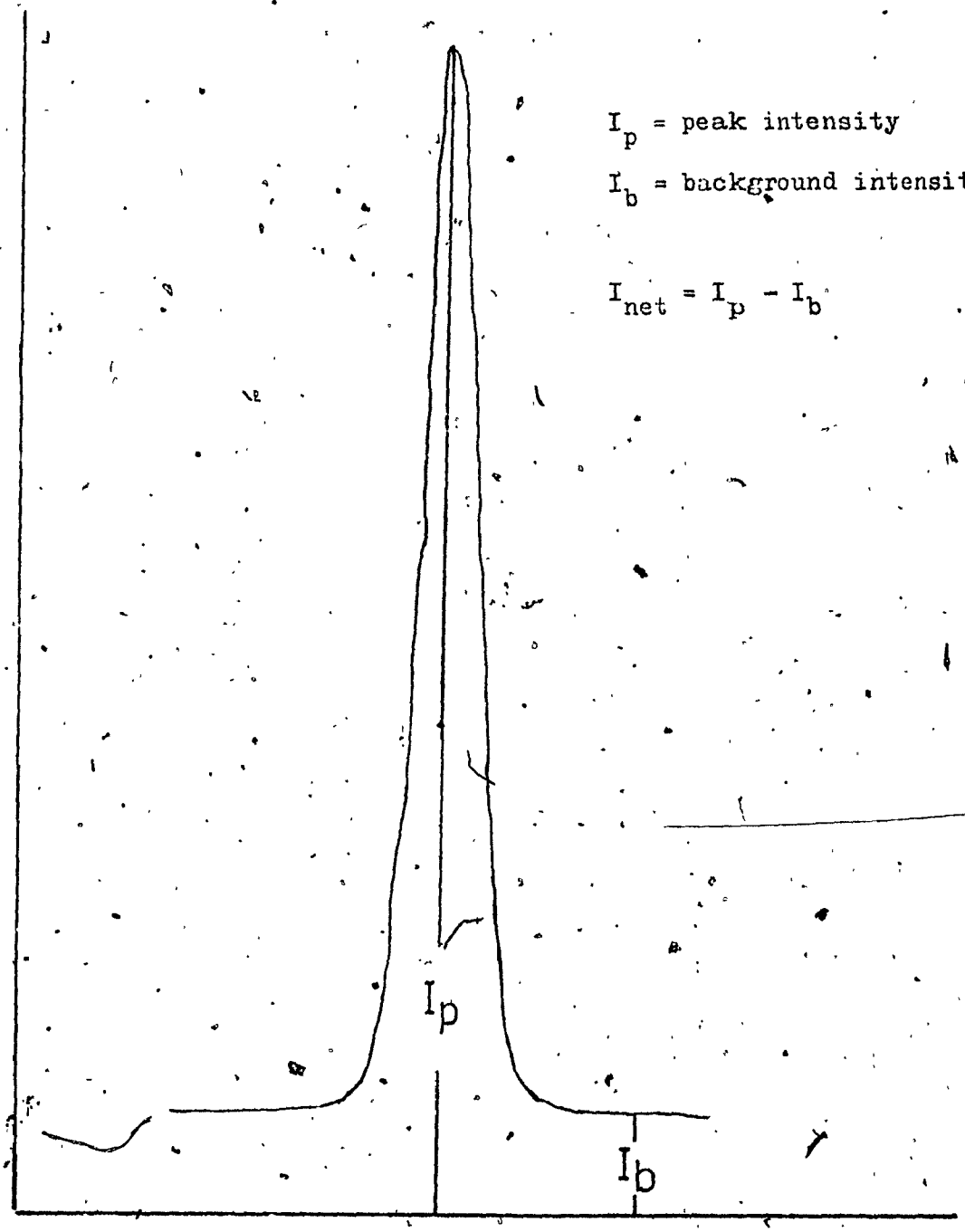
(2) an interfereing line from the tube target or from some other element in the matrix.

(3) the chloride content of the mylar film, this can affect the measured intensity for ClKα for the specimen.

Problem (1) has been handled in Section 2.3. Problems (2) and (3) were investigated by using a blank sample, and the net intensity is given as the peak intensity minus the intensity of blank sample using the same parameter for each measurement. The actual formula for the net intensity measurement may be found in Section 4.2

FIGURE 2.4

NORMAL MEASUREMENT OF NET INTENSITY



I_p = peak intensity

I_b = background intensity.

$I_{net} = I_p - I_b$

4.4.2 Calculation of α-correction coefficients.

In the earlier discussion of empirical coefficients, it was suggested that they be determined for each pair of elements by preparing binary standard systems for those elements. In this investigation, a liquid specimen was used, and a solution containing the element A is actually a binary mixture, with the aqueous matrix M as the second component. The correction coefficient for the effect of M on A can be given as Equation (17)

$$\alpha_{AM} = \frac{I_{A(2)}C_{A(1)} - I_{A(1)}C_{A(2)}}{I_{A(1)}C_{A(2)}C_{M(1)} - I_{A(2)}C_{A(1)}C_{M(2)}} \quad (17)$$

where:-

I_A = the net intensity of analyte element A.

C_A, C_M = the weight fractions of element A and aqueous matrix.

the subscripts 1 and 2 = standard solutions 1, and 2.

Where a solution contains the analyte A, another element B and the residual aqueous matrix M, it may be used to determine α_{AB} where α_{AM} is known. A series of such solutions was prepared containing a constant weight fraction of the given analyte (0.01 or 0.02) and a variable weight fraction of the element B and matrix M. α_{AB}, the interelement effect of element B on

the analyte A, was determined from Equation (18) or (19)

$$\alpha_{AB} = \frac{(I_{A(2)}C_{A(1)} - I_{A(1)}C_{A(2)}) + \alpha_{AM}(I_{A(2)}C_{A(1)}C_{M(2)} - I_{A(1)}C_{A(2)}C_{M(1)})}{I_{A(1)}C_{A(2)}C_{B(1)} - I_{A(2)}C_{A(1)}C_{B(2)}} \quad (18)$$

or

$$\alpha_{AB} = \frac{I_{A(2)} - I_{A(1)} + \alpha_{AM}(I_{A(2)}C_{M(2)} - I_{A(1)}C_{M(1)})}{-I_{A(1)}C_{B(1)} - I_{A(2)}C_{B(2)}} \quad (19)$$

(i.e. $C_{A(1)} = C_{A(2)}$)

Table 2.4 indicates in chart form the accumulated results of the total survey relative to the determination from aqueous solution media of the correction coefficients. The horizontal headings lists the elements affected. The left-hand column lists the elements in the general matrix providing the interfering effect. In this column, the heading M indicates the residual matrix combination of hydrogen-nitrogen-oxygen or, under certain circumstances, hydrogen-oxygen alone.

2.5 Experimental Results

The general process of treating experimental data is now shown, using as example the determination of the effect

TABLE 2.4

α-CORRECTION COEFFICIENTS AS DETERMINED FOR AQUEOUS SOLUTIONS

α	$Al_{(13)}$	$Cl_{(17)}$	$Mn_{(25)}$	$Fe_{(26)}$	$Ni_{(28)}$	$Cu_{(29)}$
M	1.2^{8}	-0.39^{3}	-0.852^{4}	-0.900^{5}	-0.916^{9}	-0.925^{7}
Al	----	-0.24^{8}	-0.65^{1}	-0.71^{4}	-0.79^{7}	-0.85^{9}
Cl	1.94^{3}	----	-0.37^{1}	-0.065^{1}	-0.153^{5}	-0.237^{0}
Mn	3.2^{7}	0.42^{7}	----			
Fe	5.2^{6}	0.62^{3}		----		
Ni	7.2^{1}	0.83^{7}			----	
Cu	7.4^{5}	0.90^{6}				----

of the aqueous matrix M on aluminum as a binary system, and the effect of manganese and M on aluminum as a tertiary system.

2.5.1 Binary system

Seven aluminum solutions, ranging from 0.01 to 0.03708 weight fraction of aluminum, were prepared by dilution of an aluminum stock solution which contained 0.05000 ± 0.00001 g of Al/ml. AlK_α radiation measurement was made at peak intensity, with the spectrometer operating at 50kV and 36mA, and at other appropriate parameters. The average of five counting periods, of 50 seconds counting time each was obtained. The measured AlK_α intensity was corrected for the blank sample background and for the mylar effect. This procedure is outlined in Table 2.5(a).

The results obtained from the above were then explored by Equation (17) to determine the value of α_{AlM}. The solution combinations chosen were such as to yield maximum differences in numerator and denominator values, this so as to obtain the best possible accuracy in the determination of the derived -correction coefficient value. The average value and standard deviation were also calculated. This calculation and result are shown in Table 2.5(b).

TABLE 2.5

EFFECT OF M ON AL

(a)

Solution	C_{Al}	C_M	$I^{meas.}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
A-1	0.01000	0.99000	101	398
A-2	0.01500	0.98500	152	599
A-3	0.02000	0.98000	203	801
A-4	0.02500	0.97500	255	1004
A-5	0.03000	0.97000	307	1208
A-6	0.03500	0.96500	359	1414
A-7	0.03708	0.96292	381	1499

(b)

		α_{AlM}
Solution A-1/	Solution A-7	1.18101
" A-1/	" A-6	1.16261
" A-1/	" A-5	1.13247
" A-1/	" A-4	1.18071
" A-2/	" A-7	1.38534
" A-2/	" A-6	1.37054
" A-2/	" A-5	1.41124
" A-3/	" A-7	1.39017
" A-3/	" A-6	1.38310
" A-4/	" A-7	1.18317

average α_{AlM} = 1.2^8

std. devn. = $\pm 0.1^2$

A determination of the corrected intensity for each specimen solution was made, using the equation:-

$$I^{Corr.}_{AlK\alpha} = I^{My}_{AlK\alpha}\left(1 + \alpha_{AlM}\, C_M\right) \qquad (20)$$

The value of I^{o}_{AlK} for $AlK\alpha$ radiation was calculated individually, using Equation (21). The average value was also calculated. This procedure is outlined in Table 2.5(c).

$$I^{o}_{AlK\alpha} = I^{Corr.}_{AlK\alpha} / C_{Al} \qquad (21)$$

Back calculation of the concentration of the analyte element was given by Equation (22), and all the values calculated to same significant figure position as C_{Al} (known).

$$C^{Back}_{Al} = I^{Corr.}_{AlK\alpha} / I^{o}_{Al} \qquad (22)$$

The absolute error and the relative percentage error in the concentration of the analyte element Al was calculated using the following equations:-

$$\left| C^{Back}_{Al} - C_{Al} \right| = \text{Absolute error} \qquad (23)$$

$$(\text{Absolute error})/C_{Al} \times 100 = \text{Relative percent error} \quad (24)$$

These calculations are shown in Table 2.5(d).

The measured intensity, the corrected intensity for mylar effect; and the corrected intensity for matrix effect versus the concentration of analyte element C_{Al} and the concentration of matrix C_M were plotted in Figure 2.5.

2.5.2 Tertiary system

The general processes were almost identical to those for the binary system, except for the processes of solution preparation and α-correction coefficient calculation. Six standard solutions, containing a constant aluminum weight fraction 0.08 , and a manganese weight fraction varying from 0.0000 to 0.0383, were prepared by dilution of an aluminum stock solution which contained 0.05000 ± 0.00001 g of Al/ml and a manganese stock solution which contained 0.10000 ± 0.00001 g of Mn/ml. The value of α_{AlMn} was calculated using Equation (18) or (1)). The corrected intensity was obtained from:-

$$I^{Corr.}_{AlK\alpha} = I^{My}_{AlK\alpha}(1 + \alpha_{AlM} C_M + \alpha_{AlMn} C_{Mn}) \quad (25)$$

TABLE 2.5

(c)

Solution	C_{Al}	C_M	$I^{My.}_{AlK\alpha}$ (cps)	$I^{Corr.}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
A-1	0.01000	0.99000	338	903	90325
A-2	0.01500	0.98500	599	1354	90236
A-3	0.02000	0.98000	801	1805	90244
A-4	0.02500	0.97500	1004	2257	90296
A-5	0.03000	0.97000	1208	2708	90269
A-6	0.03500	0.96500	1414	3159	90270
A-7	0.03708	0.96292	1499	3347	90270

average $I^{o}_{AlK\alpha}$ = 90270 cps

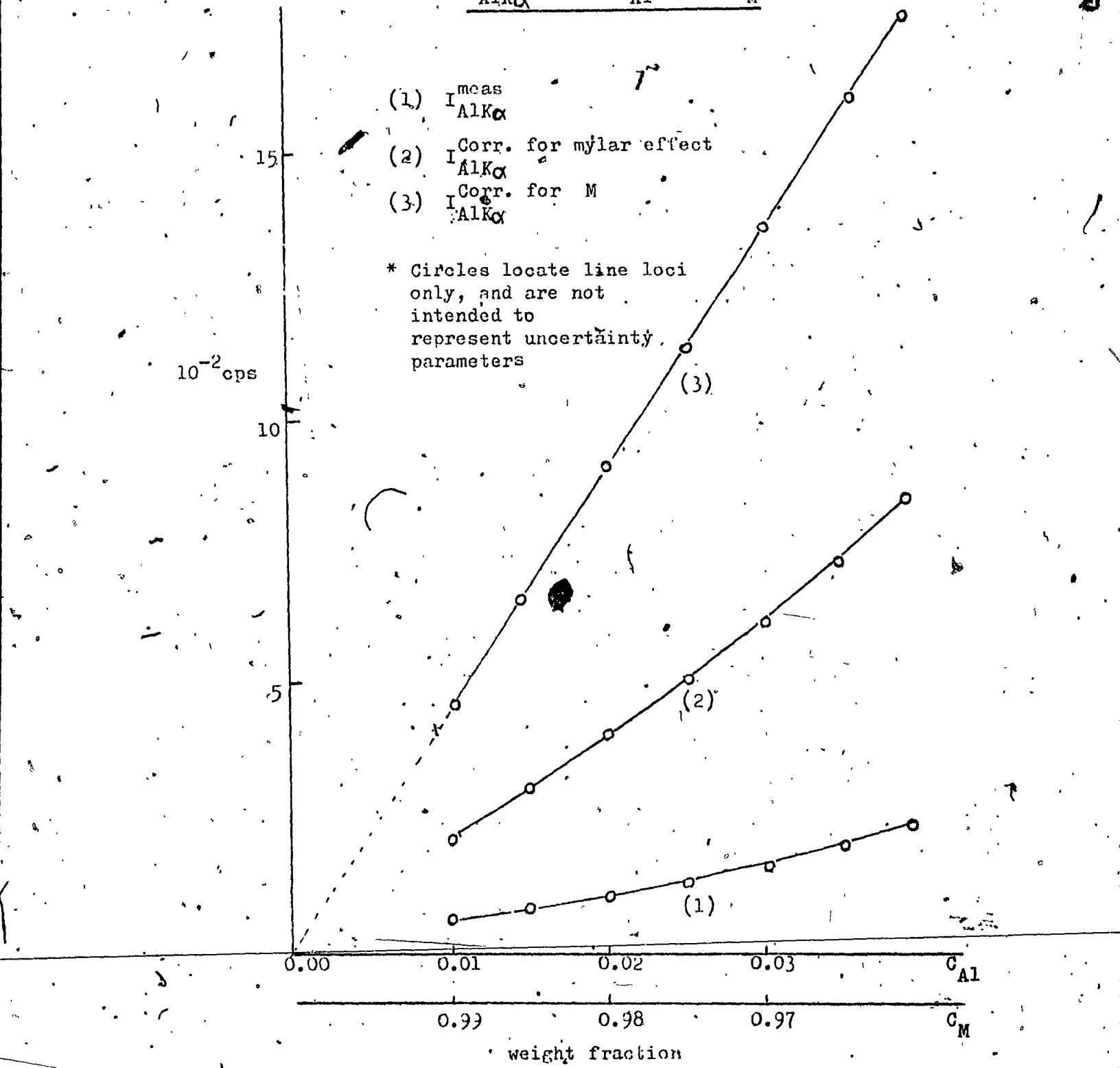
std. devn. = ± 30 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$ (cps)	C^{Back}_{Al}	Absolute error	% error
A-1	0.01000	903	0.01000	0.00000	0.0
A-2	0.01500	1354	0.01500	0.00000	0.0
A-3	0.02000	1805	0.02000	0.00000	0.0
A-4	0.02500	2257	0.02500	0.00000	0.0
A-5	0.03000	2708	0.03000	0.00000	0.0
A-6	0.03500	3159	0.03500	0.00000	0.0
A-7	0.03708	3347	0.03708	0.00000	0.0

FIGURE 2.5

$I_{AlK\alpha}$ VERSUS C_{Al} AND C_M



These calculations are shown in Tables 2.6(a), (b), (c) and (d) respectively. Calibration curves are plotted, as shown in Figure 2.6, using the measured intensity, the corrected intensity for mylar effect, the corrected intensity for matrix M effect and the corrected intensity of analyte Al versus the concentration of effecting element Mn and aqueous matrix M.

All of the data from this investigation may be found in the tables and figures of Sections 4.1 and 4.2 .

TABLE 2.6.

EFFECT OF M AND MN ON AL

(a)

Solution	C_{Al}	C_{Mn}	C_M	$I^{meas}_{AlK\alpha}$(cps)	$I^{My}_{AlK\alpha}$(cps)
AM-1	0.02000	0.00000	0.98000	178	700
AM-2	0.02000	0.01500	0.96500	176	694
AM-3	0.02000	0.02000	0.96000	175	690
AM-4	0.02000	0.02500	0.95500	174	685
AM-5	0.02000	0.03000	0.95000	173	681
AM-6	0.01915	0.03830	0.94255	165	650

(b)

	α_{AlMn}	
Solution AM-1/Solution AM-6	3.08334	
" AM-1/ " AM-5	3.40971	
" AM-1/ " AM-4	3.30761	
" AM-2/ " AM-6	4.17092	(reject)
" AM-2/ " AM-5	4.11317	(reject)
" AM-3/ " AM-6	3.29494	

average α_{AlMn} = 3.2?

std. devn. = $\pm$ 0.3^0

(c)

Solution	C_{Al}	C_{Mn}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{Corr.}_{AlK\alpha}$	$I^{o}_{AlK\alpha}$
AM-1	0.02000	0.00000	0.98000	700	1579	1579	78938
AM-2	0.02000	0.01500	0.96500	694	1550	1584	79216
AM-3	0.02000	0.02000	0.96000	690	1539	1584	79198
AM-4	0.02000	0.02500	0.95500	685	1522	1578	79182
AM-5	0.02000	0.03000	0.95000	681	1509	1576	78904
AM-6	0.01915	0.03830	0.94255	650	1435	1516	79182

average $I^{o}_{AlK\alpha}$ = $7.90^{4} \times 10^{4}$ cps

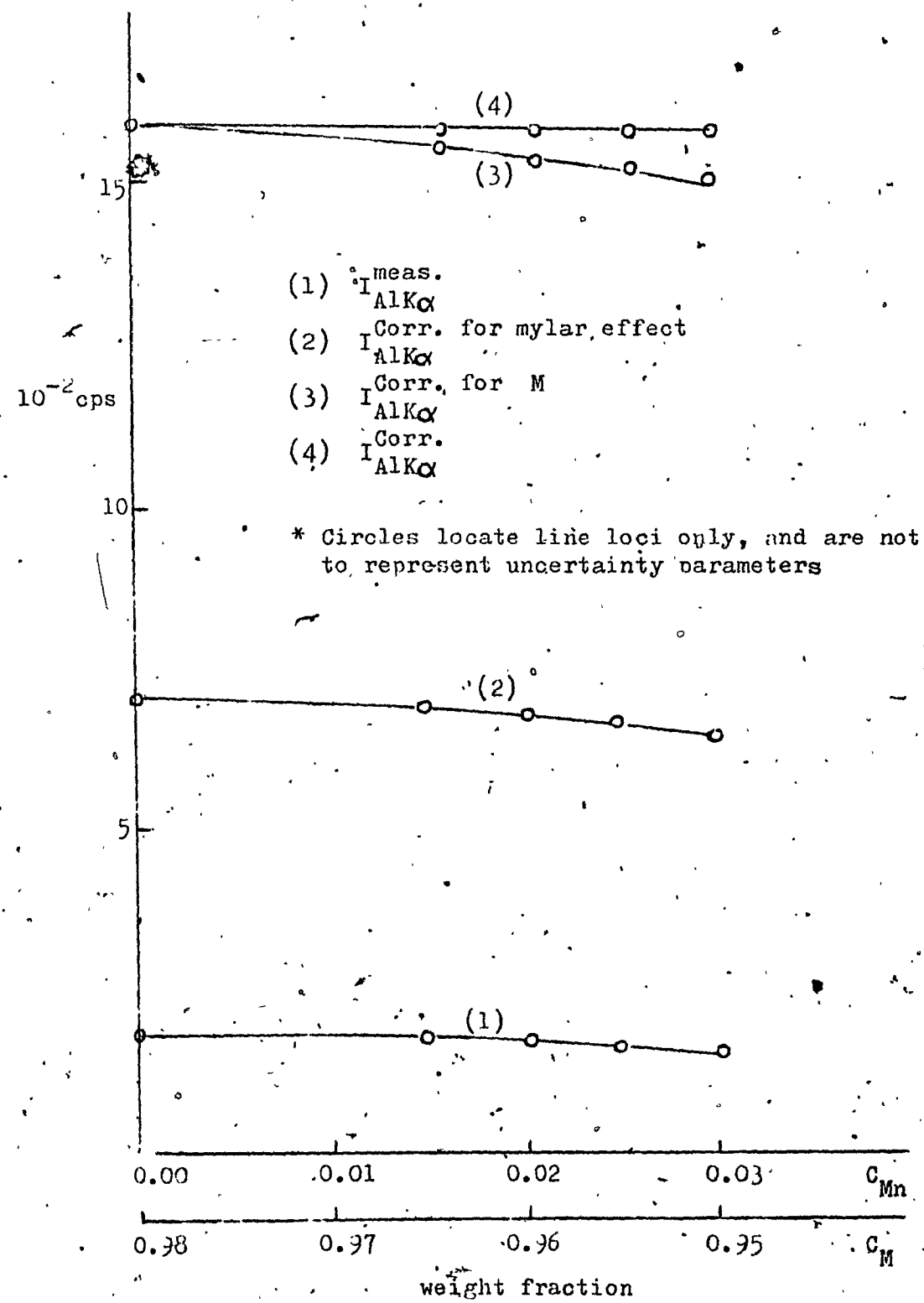
std. devn. = $0.01^{8} \times 10^{4}$ cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$ (cps)	C^{Back}_{Al}	Absolute error	% error
AM-1	0.02000	1579	0.01998	0.00002	0.10
AM-2	0.02000	1584	0.02004	0.00004	0.20
AM-3	0.02000	1584	0.02004	0.00004	0.20
AM-4	0.02000	1578	0.01996	0.0000	0.20
AM-5	0.02000	1576	0.01994	0.00006	0.30
AM-6	0.01915	1516	0.01918	0.00003	0.16

FIGURE 2.6

$I_{AlK\alpha}$ VERSUS C_{Mn} AND C_M



3. CONCLUSION

The method of approach was aimed at exploring the use of XRF in the analysis of aqueous solutions representing metal alloys, particularly commercial aluminum alloys of unkown composition. A subsequent analytical applications program is planned to:-

(1) Determination the interelement-effect correction coefficients for other relevant elements; such as magnesium, silicon, titanium, etc.

(2) Apply the determined α-correction coefficients in the analysis of commercial aluminum alloys.

Uncertainties for the α-Correction Coefficients Determination

These are often somewhat high on account of the low emission intensities and high background corrections for some of the determinations. Both factors lead to comparatively high relative uncertainties for the calculated coefficients.

Where long-wavelength radiation is involved, the effects of mylar films, based on composition and thickness, requires careful correction.

Constancy of the α-Correction Coefficient

Lachance[24] has shown that, where the concentration of the analyte is approximately 10 percent or less by weight fraction, the α-correction coefficients for the interelement effects remain constant and reasonably independent of instrumental geometry. In certain instances, however, second order correction term may have to be applied and the concentration of the analyte sould be considered. Both are referred to in Appendix I and II.

Effects of Chlorine, Sulfur and Phosphorus

In the investigation now planned, hydrochloric acid, sufuric acid and phosphoric acid will often be required to permit the dissolving of aluminum alloys containing elements such as titanium, silicon, etc. It is aporeciated that the effects of the aqueous matrix on sulfur and phosphorus must be determined in the subsequent analytical program, as must their effects on the analytes of interest.

4. DATA PRESENTATION

The experimental data to be presented, consist of the following two sections:-

4.1. The absorptive effect of mylar film coverings for XRF analysis.

4.2. The interelement effect in the XRF analysis.

4.1 Absorptive Effect of Mylar Film Coverings

Tables involving "Intensity Measurement" and " k Value Determination"

Using different thicknesses for the mylar film covering, the K_α radiation for elements of atomic number 12 to 30 were measured. The parameter for each determination is shown in Table 4.1.

The k value may be calculated by Equation (14) or (15):-

$$k = \frac{\ln I_o - \ln I_x}{x} \qquad (14)$$

$$k = \frac{\ln I_2 - \ln I_1}{x_1 - x_2} \qquad (15)$$

The average value of k was calculated, and the standard deviation was also given.

Figures involving "$I_{AK\alpha}$ Versus Thickness of Mylar Covering"

The intensity of analyte A versus the thickness of mylar covering, was plotted on this figure and the circles surrounding each experimentally determined locus on a curve are for identification of the locus only, they do not reflect the uncertainty

parameters around the locus.

TABLE 4.1

EXPERIMENTAL PARAMETERS FOR XRF ANALYSIS

ELEMENT	TUBE TARGET	ANALYZING CRYSTAL	COLLIMATOR	COUNTER	2θ DEGREE
Mg	Cr 50 kV 36 mA	ADP	COARSE	PF	136.69
Al	Cr 50 kV 36 mA	PET	COARSE	PF	145.28
Si	Cr 50 kV 36 mA	PET	COARSE	PF	109.31
P	Cr 50 kV 36 mA	PET	COARSE	PF	89.66
S	Cr 50 kV 36 mA	PET	COARSE	PF	75.95
Cl	Cr 50 kV 36 mA	PET	COARSE	PF	65.60
Ca	Cr 50 kV 36 mA	LiF	COARSE	PF	113.13
Ti	Cr 50 kV 36 mA	LiF	COARSE	PF	86.12
V	Cr 50 kV 36 mA	LiF	COARSE	PF	76.87
Cr	W 50 kV 20 mA	LiF	FINE	SCIN.	69.40
Mn	W 50 kV 20 mA	LiF	FINE	SCIN.	62.96
Fe	W 50 kV 0 mA	LiF	FINE	SCIN.	57.52
Co	W 50 kV 20 mA	LiF	FINE	SCIN.	52.77
Ni	W 50 kV 20 mA	LiF	FINE	SCIN.	48.64
Cu	W 50 kV 20 mA	LiF	FINE	SCIN.	45.01
Zn	W 50 kV 20 mA	LiF	FINE	SCIN.	41.78

TABLE 4.1.1

ABSORPTIVE EFFECT OF MYLAR COVERING FOR MgK_α

Thickness (10^5 inches)	I_{MgK_α} (cps)	k
0	1509	
15	385	0.209543
25	187	0.192234
30	114	0.197994
45	48	0.176223
50	34	0.175218

average k = 0.190^2

std. devn. = $\pm 0.008^5$

FIGURE 4.1.1

I_{MgK_α} VERSUS THICKNESS OF MYLAR COVERING

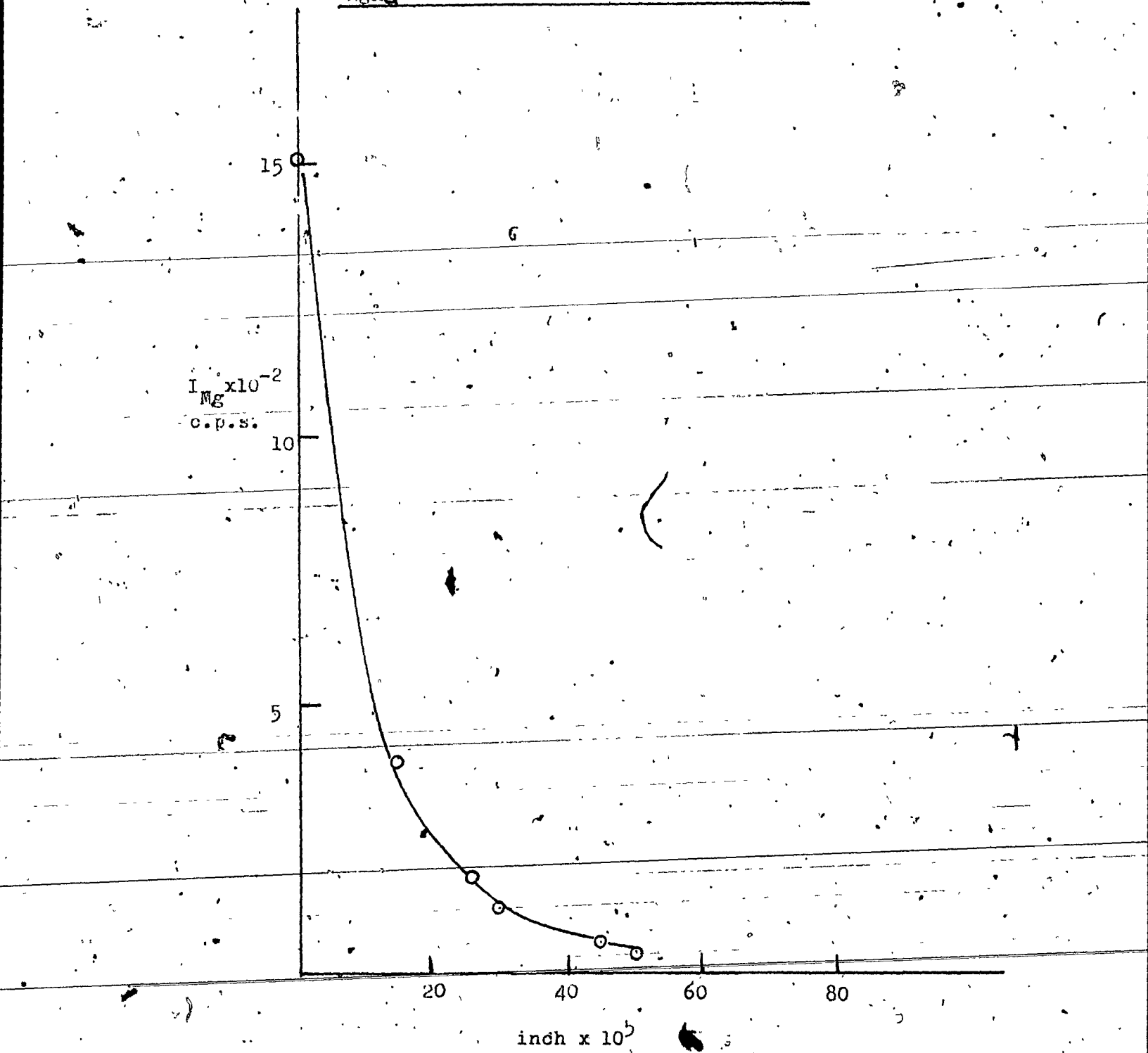


TABLE 4.1.2

ABSORPTIVE EFFECT OF MYLAR COVERING FOR AlK_α

Thickness (10^5 inches)	I_{AlK_α} (cps)	k
0	93428	
15	41183	0.12575
25	23235	0.12817
30	18044	0.12621
45	8038	0.12552
50	6027	0.12623
75	1575	0.12535

average k = 0.1262^0

std. devn. = $\pm$ 0.0006

FIGURE 4.1.2

$I_{AlK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

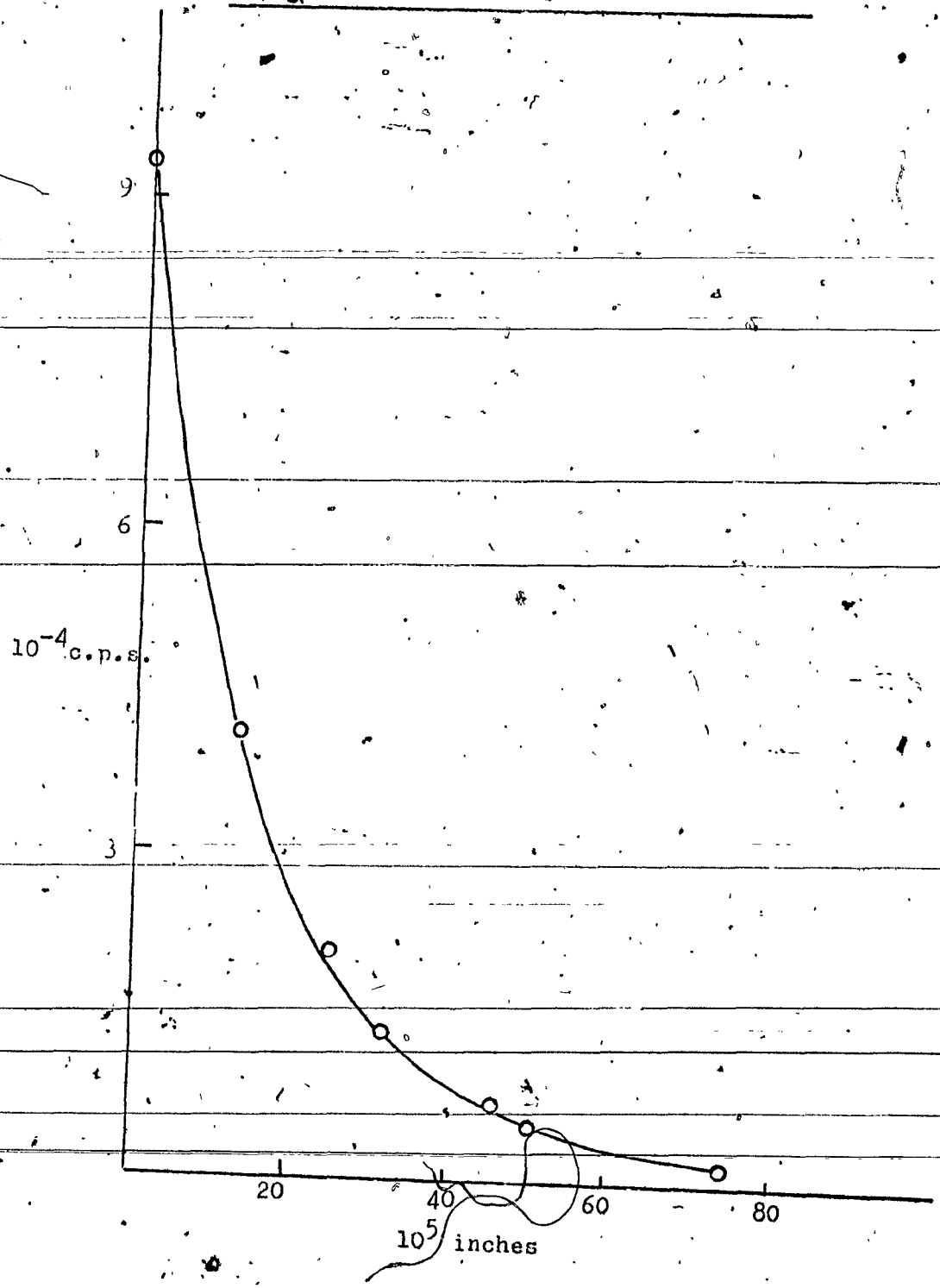


TABLE 4.1.3

ABSORPTIVE EFFECT OF MYLAR COVERING FOR SiKα

Thickness (10^5 inches)	$I_{SiK\alpha}$ (cps)	k	
0	13850		
15	8665	0.07200	(reject)
25	5723	0.08139	
30	4930	0.07928	
45	3310	0.07322	(reject)
50	2503	0.07879	
75	1067	0.07870	

average k = 0.0735^4

std. devn. = $\pm 0.0009^2$

FIGURE 4.1.3

$I_{SiK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

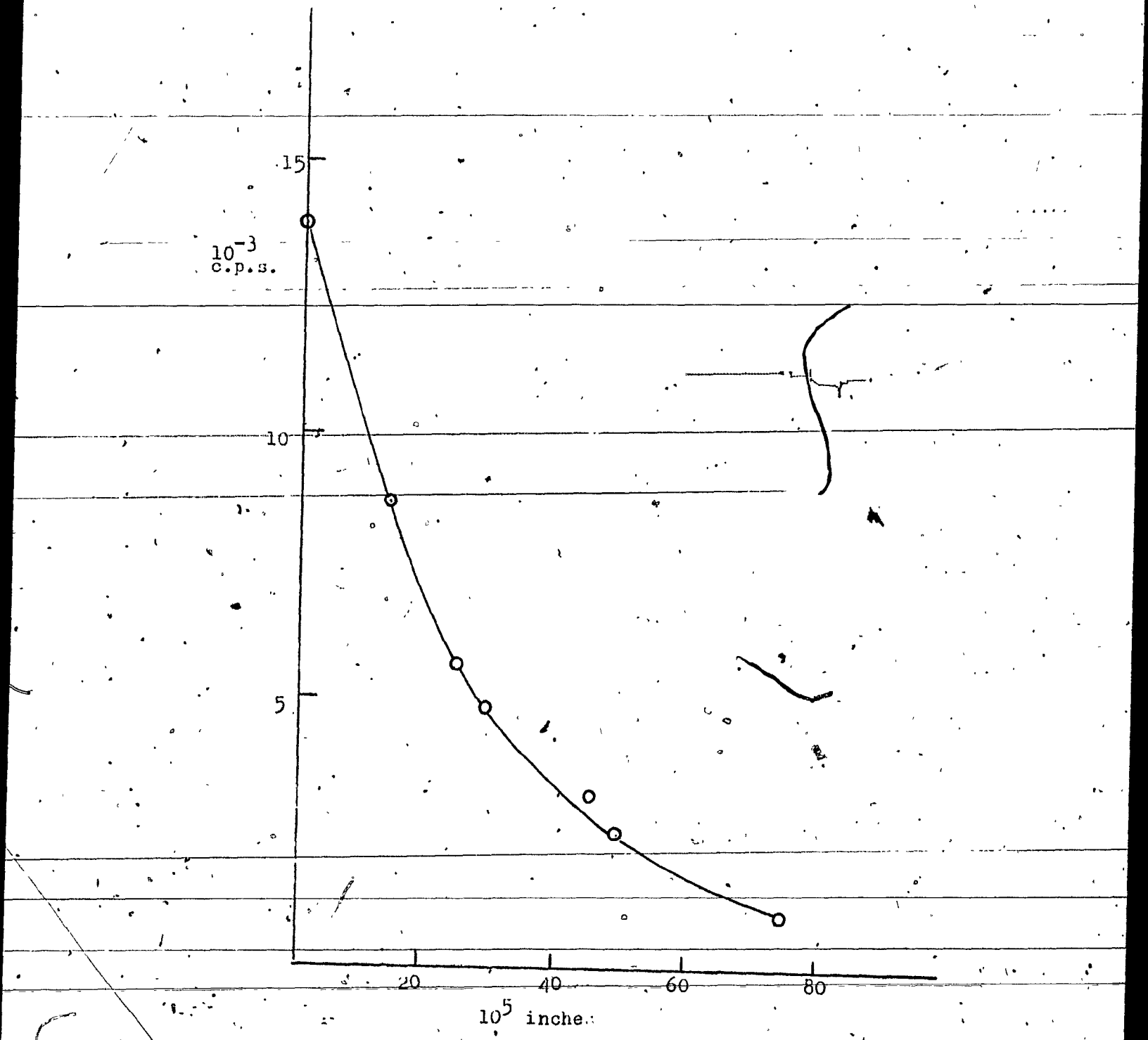


TABLE 4.1.4

ABSORPTIVE EFFECT OF MYLAR COVERING FOR $PK\alpha$

Thickness (10^{-5} inches)	$I_{PK\alpha}$ (cps)	k
0	20195	
15	14348	0.04618
25	11929	0.04849
30	11119	0.04580
45	7715	0.04924
50	7236	0.04727
75	4282	0.04762

average k = 0.0474^3

std. devn. = $\pm 0.0009^8$

FIGURE 4.1.4

I_{PK_α} VERSUS THICKNESS OF MYLAR COVERING

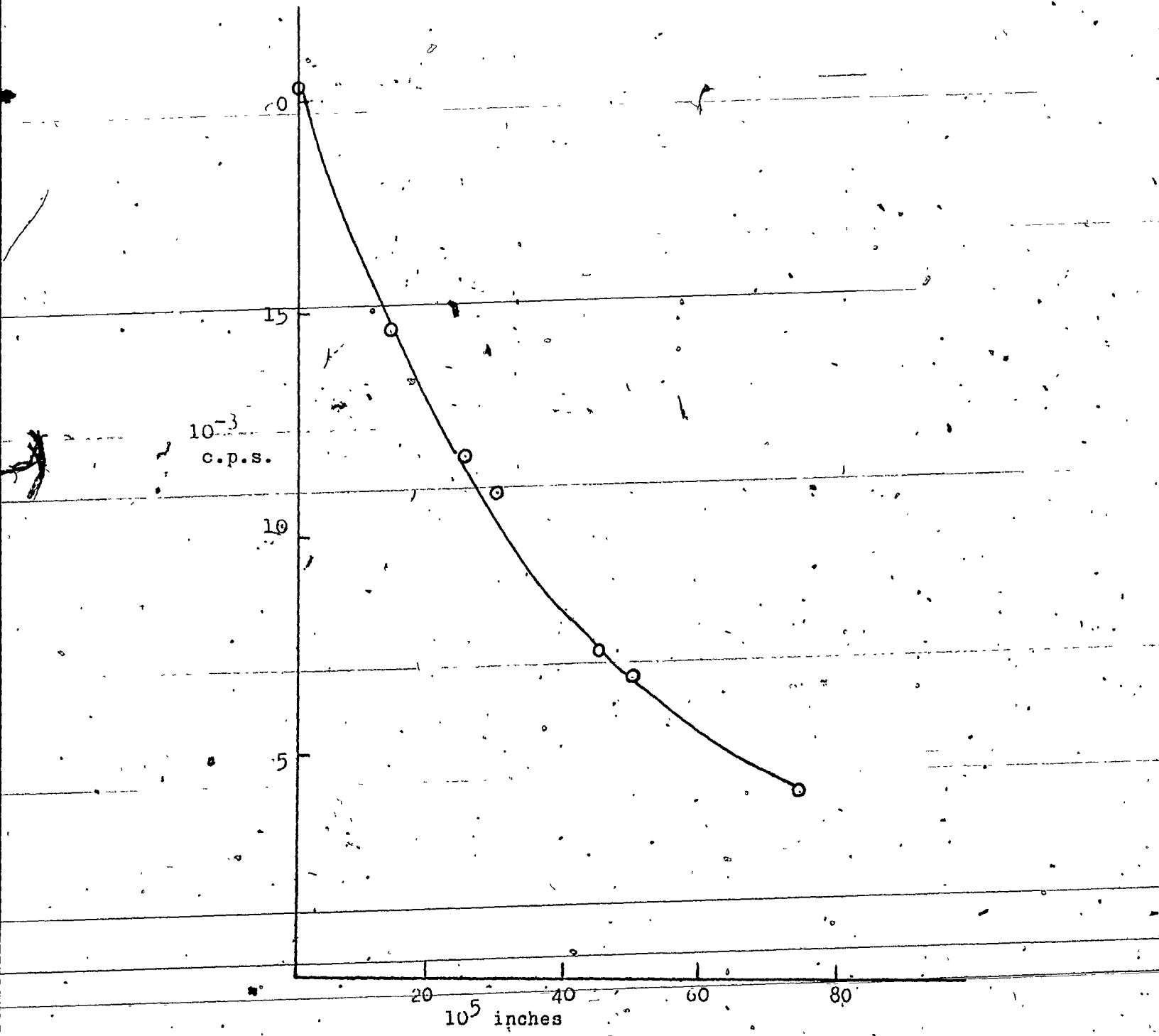


TABLE 4.1.5

ABSORPTIVE EFFECT OF MYLAR COVERING FOR SK_α

Thickness (10^5 inches)	I_{SK_α} (cps)	k	
0	134998		
15	117427	0.02140	(reject)
25	94567	0.03278	
30	87357	0.03341	
45	71632	0.03243	
50	64224	0.03420	
75	42548	0.03543	(reject)

average k = 0.03321

std. devn. = $\pm$ 0.0006

FIGURE 4.1.5

$I_{SK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

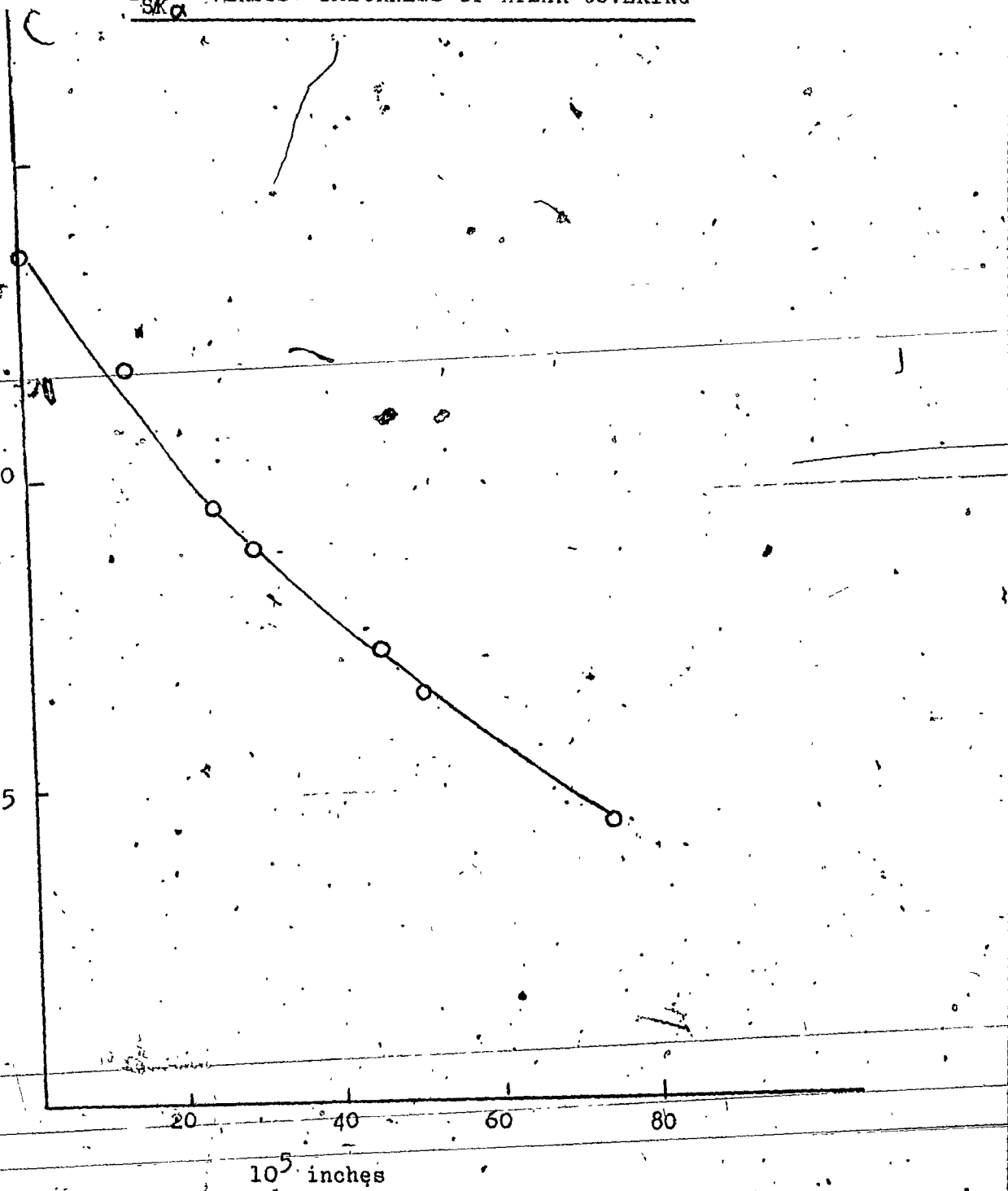


TABLE 4.1.6

ABSORPTIVE EFFECT OF MYLAR COVERING FOR $ClK\alpha$

Thickness (10^5 inches)	$I_{ClK\alpha}$ (cps)	k
0	132626	
15	117401	0.01872
25	103743	0.02262
30	92181	0.02792 (reject)
45	82879	0.02406
50	81852	0.02222
75	64213	0.02227

average k = 0.0219

std. devn. = ± 0.0019

FIGURE 4.1.6

$I_{ClK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

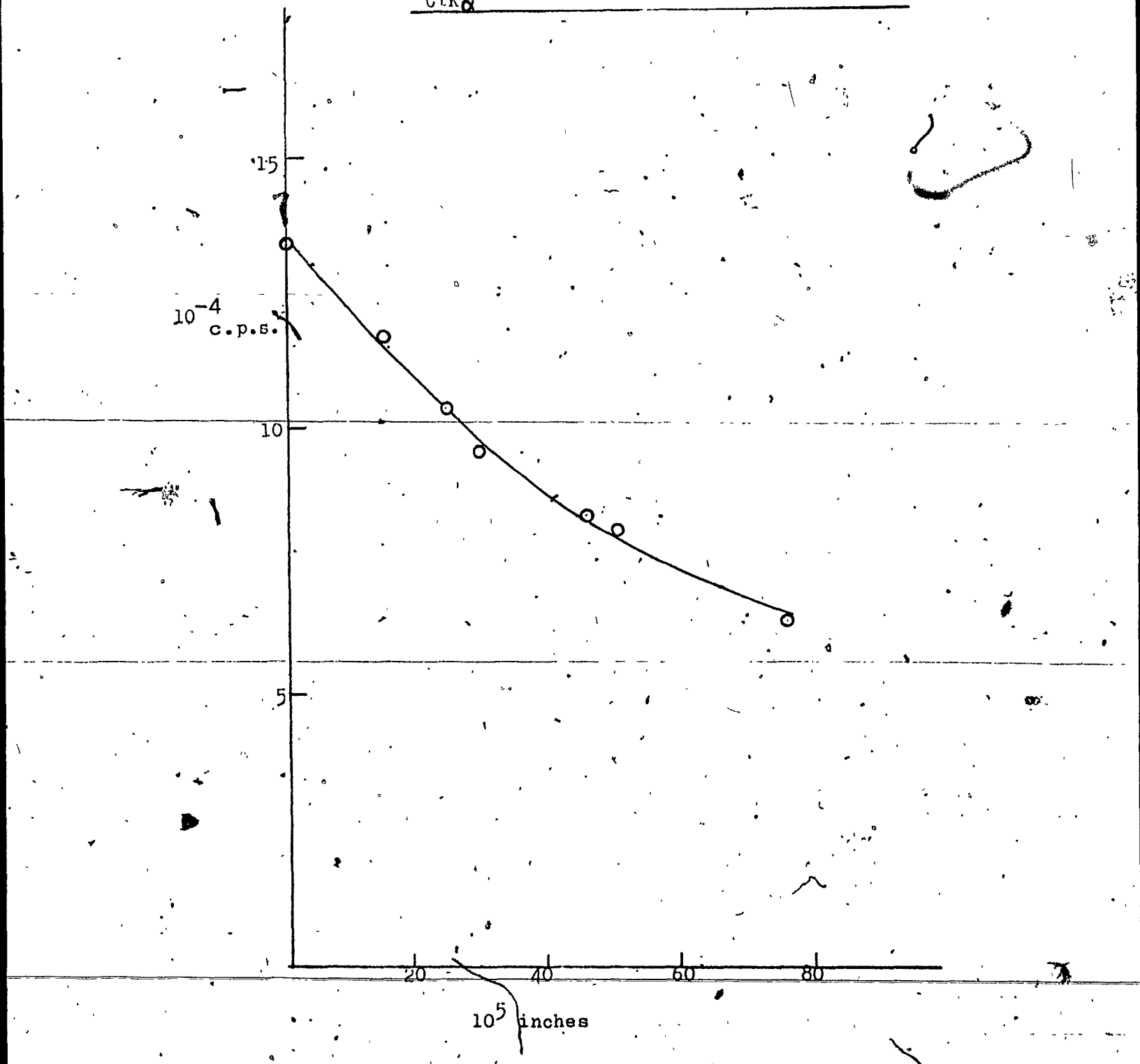


TABLE 4.1.7

ABSORPTIVE EFFECT OF MYLAR COVERING FOR CaK_α

Thickness (10^5 inches)	I_{CaK_α} (cps)	k
0	251810	
15	237154	0.009205
25	227341	0.009415
30	224531	0.008801
45	209168	0.009494
50	206035	0.009239
75	187809	0.009003

average k = 0.00919

std. devn. = ±0.00023

FIGURE 4.1.7

ABSORPTIVE EFFECT OF MYLAR-COVERING FOR CaK$_\alpha$ LINE

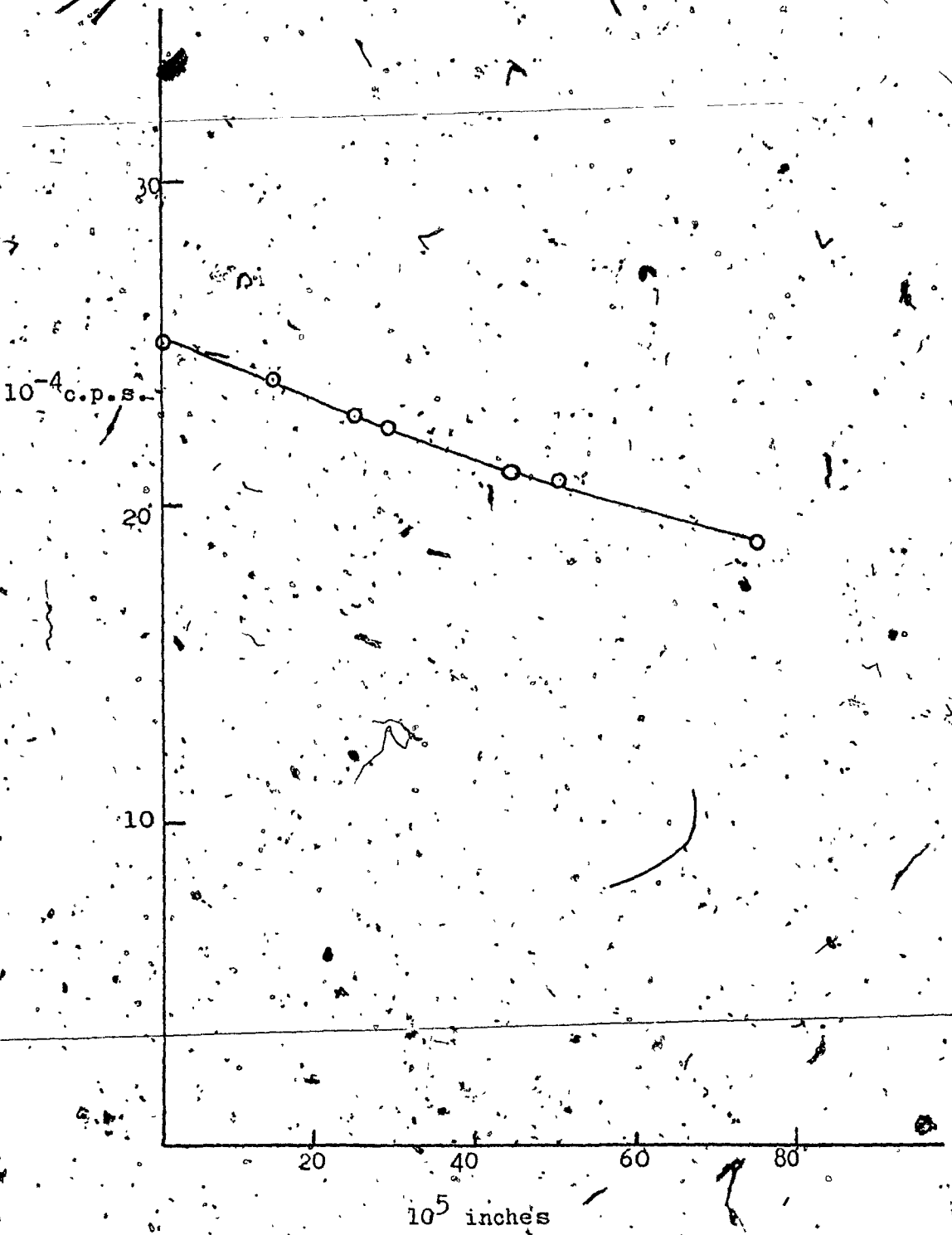


TABLE 4.1.8

ABSORPTIVE EFFECT OF MYLAR COVERING FOR TiK_α

Thickness (10^{-5} inches)	I_{TiK_α} (cps)	k
0	242151	
15	234606	0.004859
25	229823	0.004813
30	227810	0.004686
45	219893	0.005050
50	218212	0.004794
75	208080	0.004656

average k = 0.00480^9

std. devn. = $\pm\ 0.00009^8$

FIGURE 4.1.8

$I_{TiK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

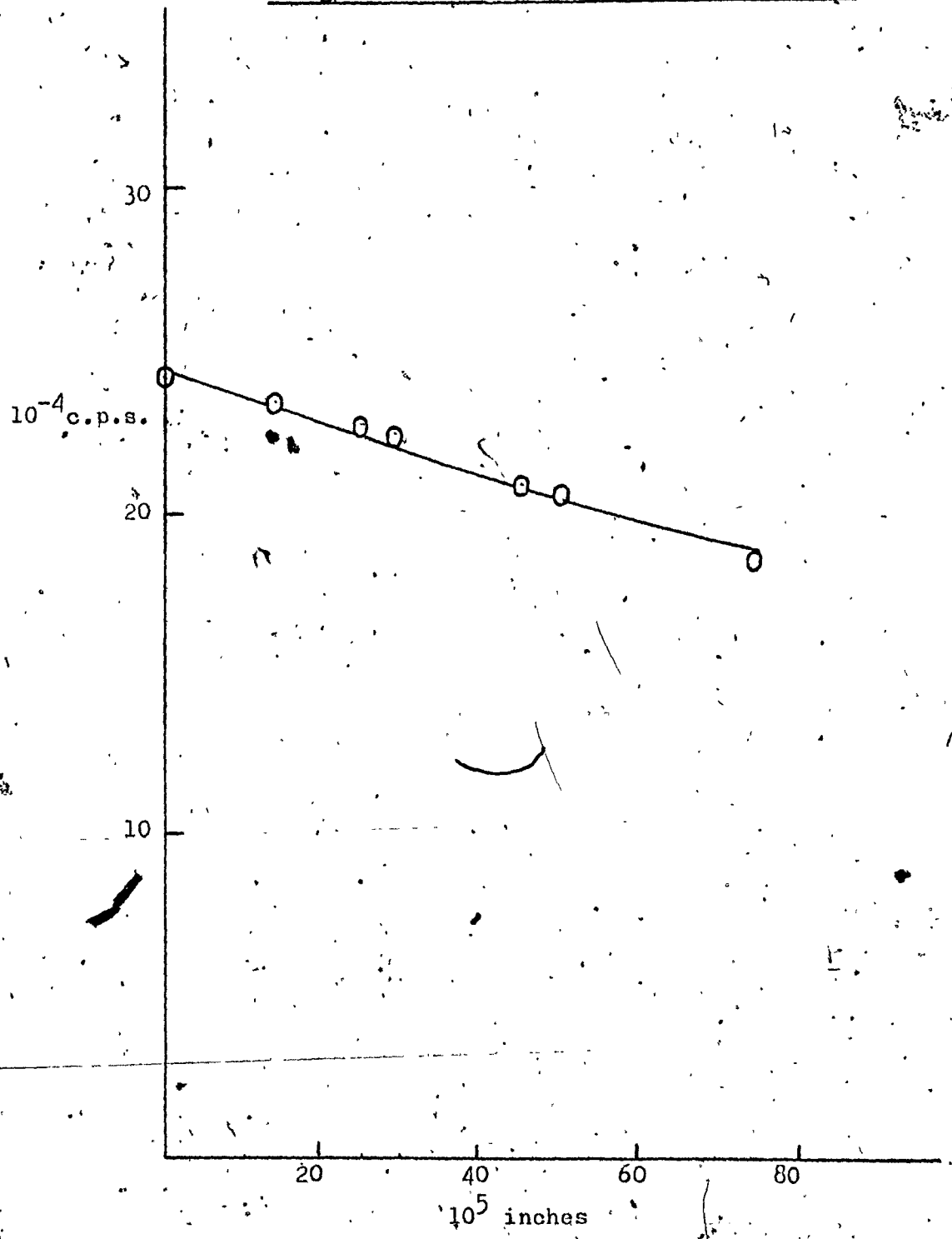


TABLE 4.1.3

ABSORPTIVE EFFECT OF MYLAR COVERING FOR VK_α LINE

Thickness (10^{-5} inches)	I_{VK} (cps)	k
0	198103	
15	192504	0.004469
25	188392	0.004377
30	185729	0.004984
45	179613	0.005036
50	177185	0.004643
75	167156	0.005228

average k = 0.0047

std. devn. = ± 0.0002

FIGURE 4.1.9

$I_{VK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

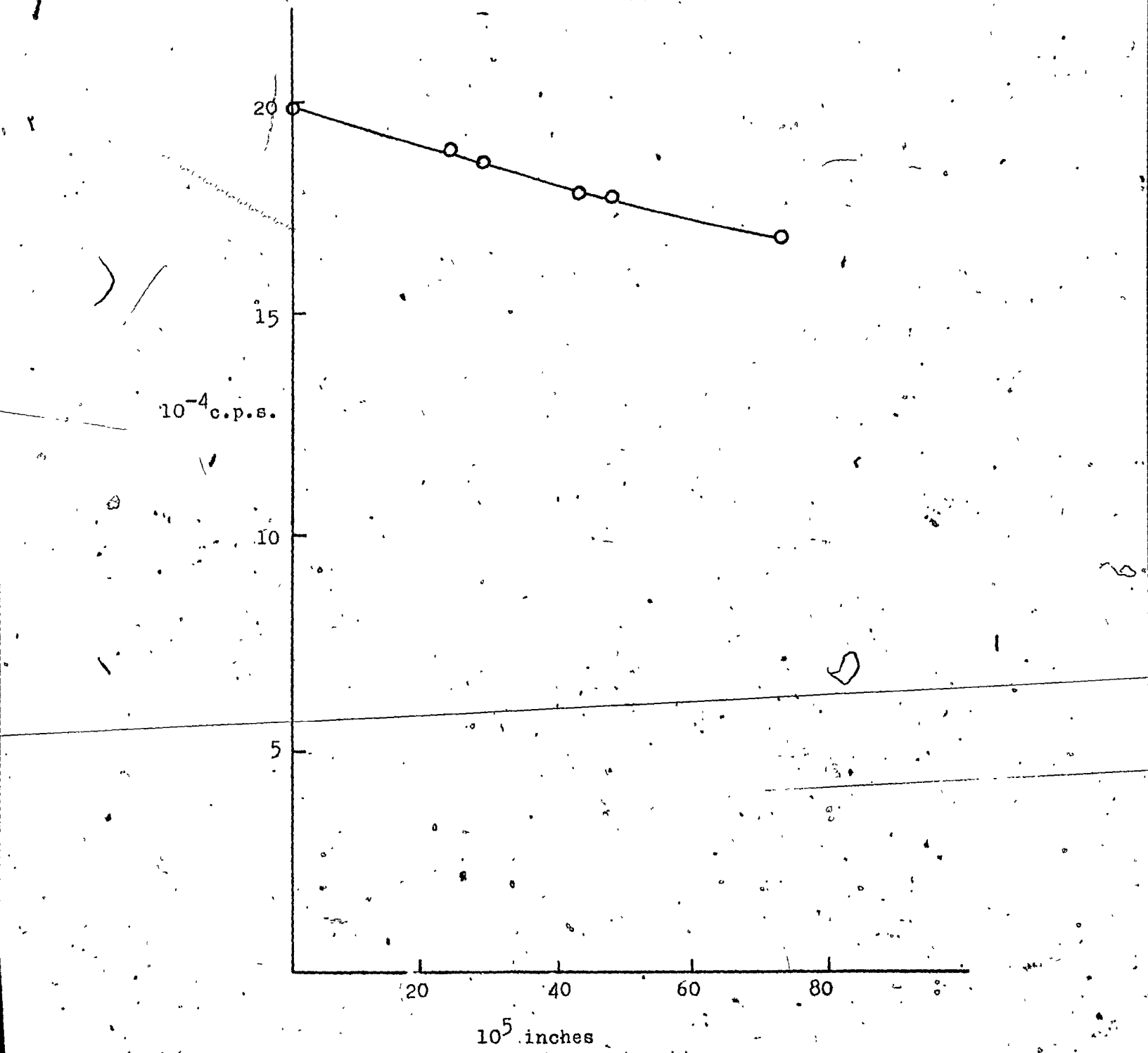


TABLE 4.1.10

ABSORPTIVE EFFECT OF MYLAR COVERING FOR CrK_α LINE

Thickness (10^5 inches)	I_{CrK_α} (cps)	k
0	68150	
15	66803	0.003065
25	65955	0.003014
30	65580	0.002950
45	64275	0.002954
50	63809	0.003031
75	61906	0.002950

average k = 0.00300^1

std. devn. = $\pm 0.00003^6$

FIGURE 4.1.10

$I_{CrK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

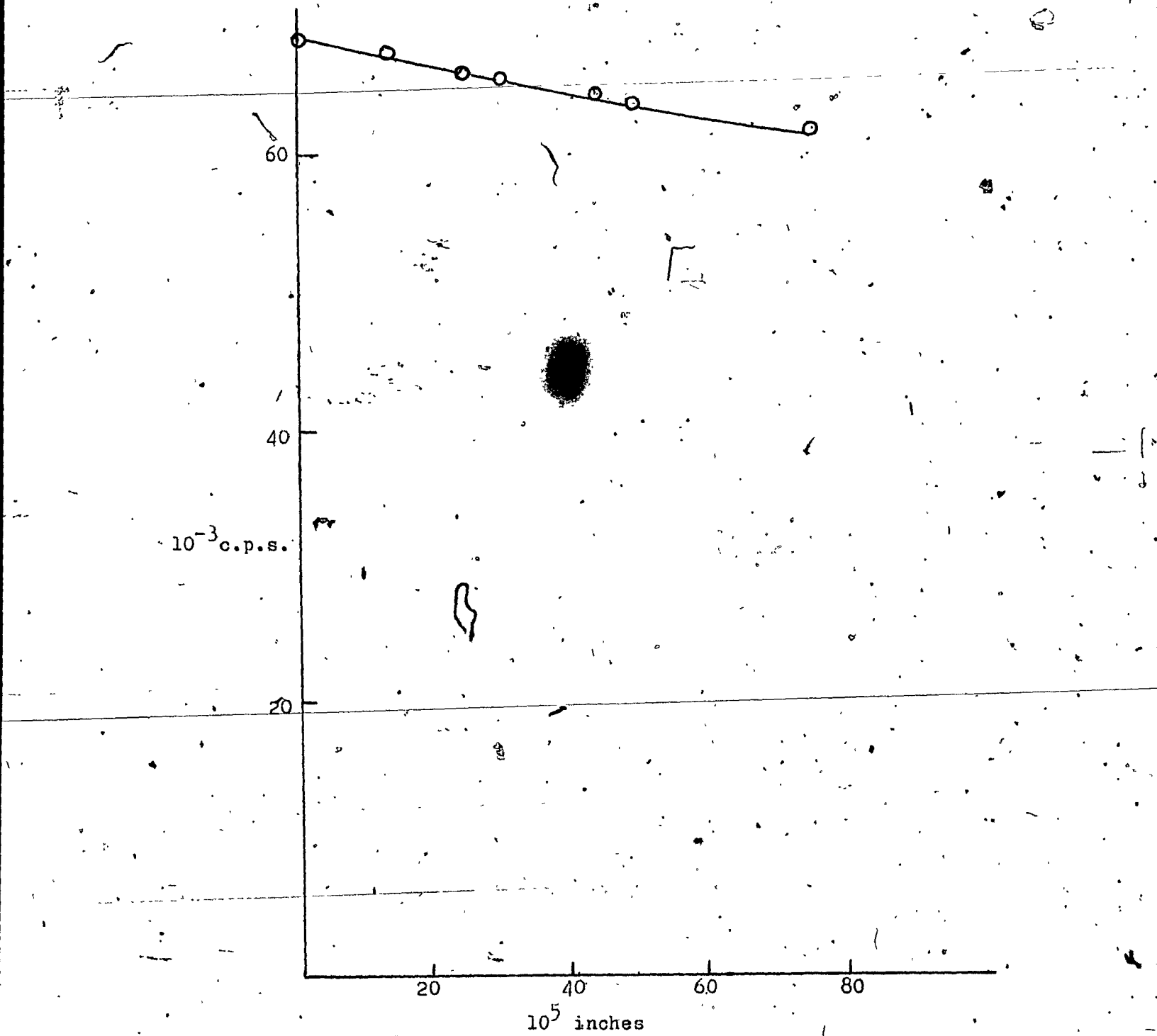


TABLE 4.1.11

ABSORPTIVE EFFECT OF MYLAR COVERING FOR $MnK\alpha$

Thickness (10^5 inches)	$I_{MnK\alpha}$ (cps)	k
0	85692	
15	84583	0.001999
25	83894	0.001953
30	83468	0.002018
45	82378	0.002018
50	81840	0.002120
75	80074	0.002082

average k = 0.00203^1

std. devn. = $\pm 0.00004^6$

FIGURE 4.1.11

$I_{MnK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

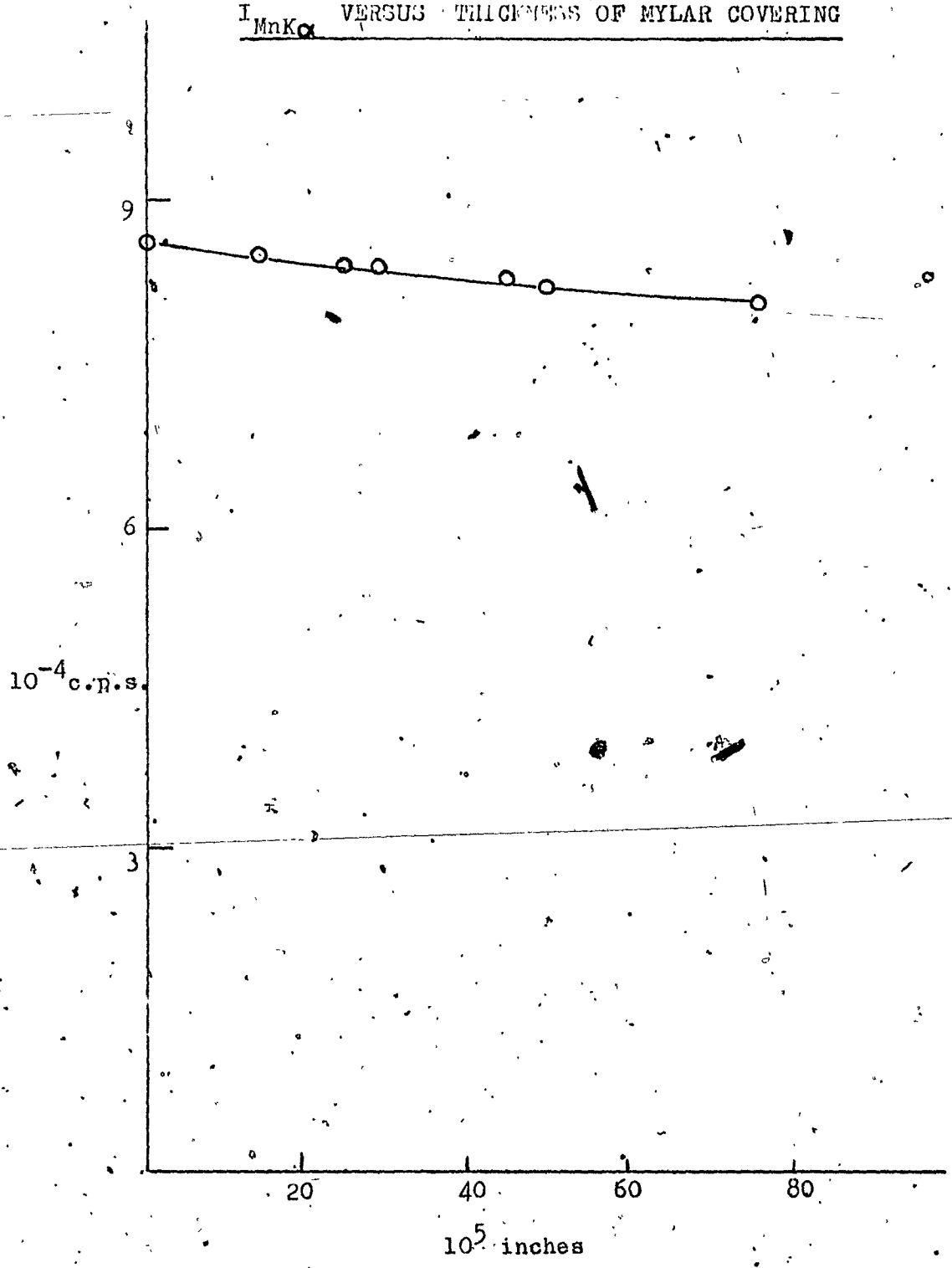


TABLE 4.1.12

ABSORPTIVE EFFECT OF MYLAR COVERING FOR FeK_α

Thickness (10^{-5} inches)	I_{FeK_α} (cps)	k
0	161600	
15	159958	0.001568
25	158728	0.001652
30	157883	0.001783
45	156236	0.001727
50	155402	0.001801
75	153134	0.001652

average k = 0.00167

std. devn. = $\pm$ 0.000073

FIGURE 4.1.12

I_{FeK_α} VERSUS THICKNESS OF MYLAR COVERING

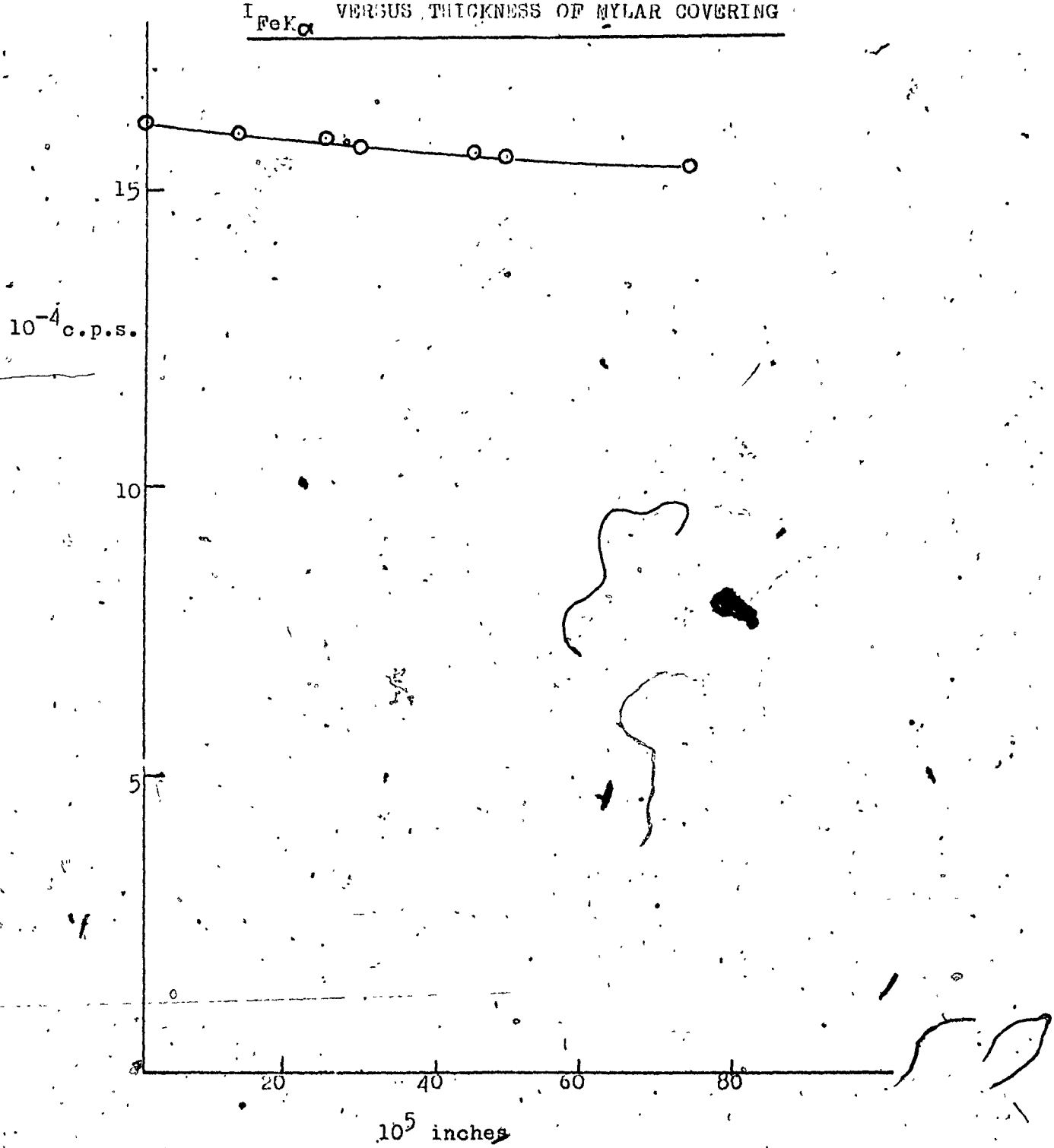


TABLE 4.1.13

ABSORPTIVE EFFECT OF MYLAR COVERING FOR $CoK\alpha$

Thickness (10^5 inches)	$I_{CoK\alpha}$ (cps)	k
0	228285	
15	226296	0.001343
25	224798	0.001418
30	224409	0.001343
45	222568	0.001298
50	222243	0.001235
75	219049	0.001268

average k = 0.00131^3

std. devn. = $\pm 0.00005^1$

FIGURE 4.1.13

$I_{CoK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

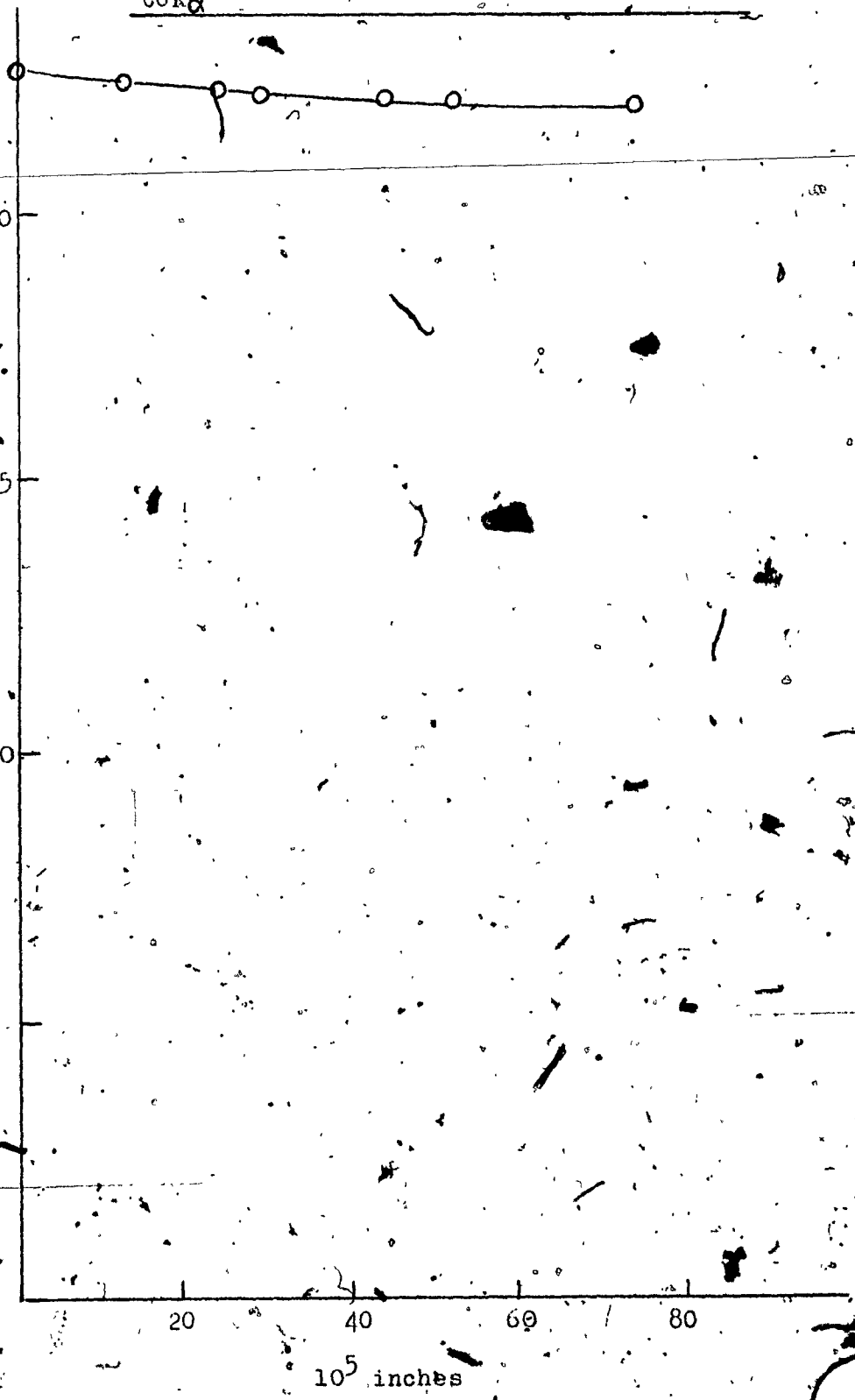


TABLE 4.1.14

ABSORPTIVE EFFECT OF MYLAR COVERING FOR NiK_α LINE

Thickness (10^5 inches)	I_{NiK_α} (cps)	k
0	279211	
15	277493	0.0009167
25	276487	0.0009031
30	275684	0.0009756
45	274416	0.0008863
50	274028	0.0008628
75	270924	0.0009249

average k = 0.000917

std. devn. = ± 0.000028

FIGURE 4.1.14

$I_{NiK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

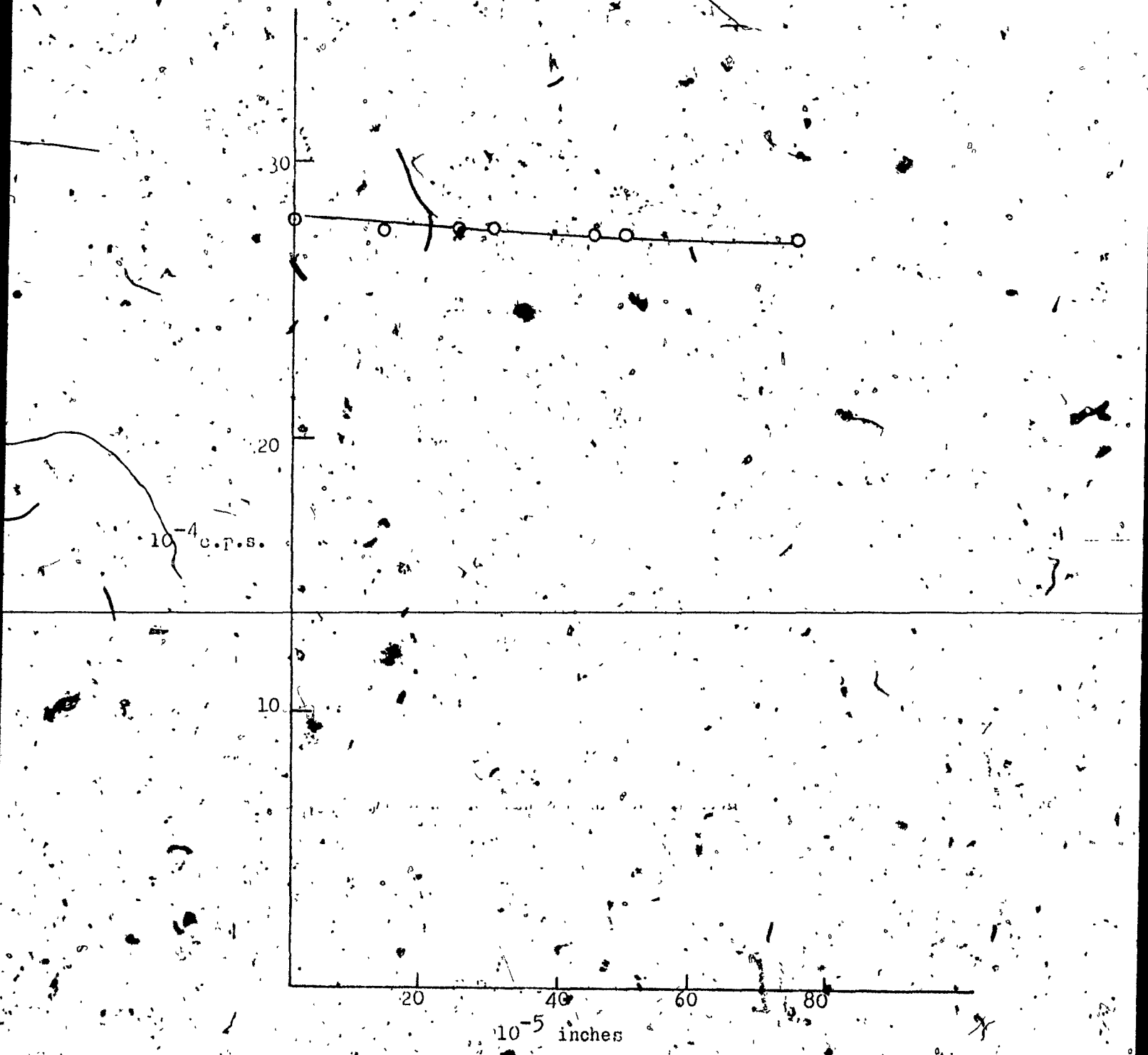


TABLE 4.1.15

ABSORPTIVE EFFECT OF MYLAR COVERING FOR CuK_α LINE

Thickness (10^{-5} inches)	I_{CuK_α} (cps)	k
0	269326	
15	268156	0.0006683
25	267424	0.0006527
30	266888	0.0006979
45	265524	0.0007240
50	265345	0.0006858
75	263097	0.0007184

average k = 0.0006911

std. devn. = $\pm$ 0.00002^2

FIGURE 4.1.15

$I_{CuK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

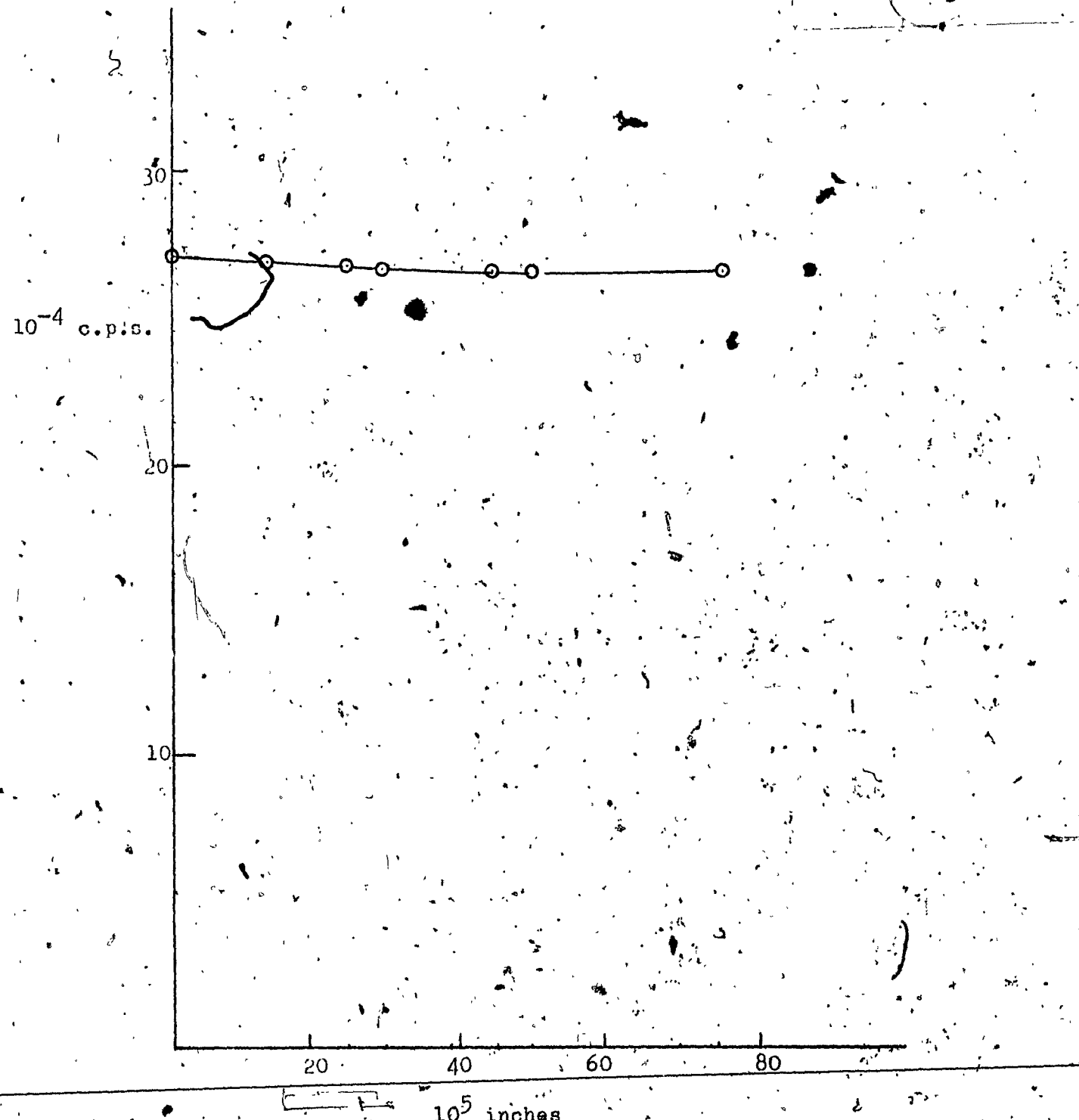


TABLE 4.1.16

ABSORPTIVE EFFECT OF MYLAR COVERING FOR ZnK_{α}

Thickness (10^5 inches)	$I_{ZnK_{\alpha}}$ (cps)	k
0	378987	
15	377846	0.0004628
25	377108	0.0004578
30	376571	0.0004909
45	375205	0.0005132
50	374807	0.0005107
75	372626	0.0005137

average k = 0.00049^3

std. devn. = 0.00002^2

FIGURE 4.1.16

$I_{ZnK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

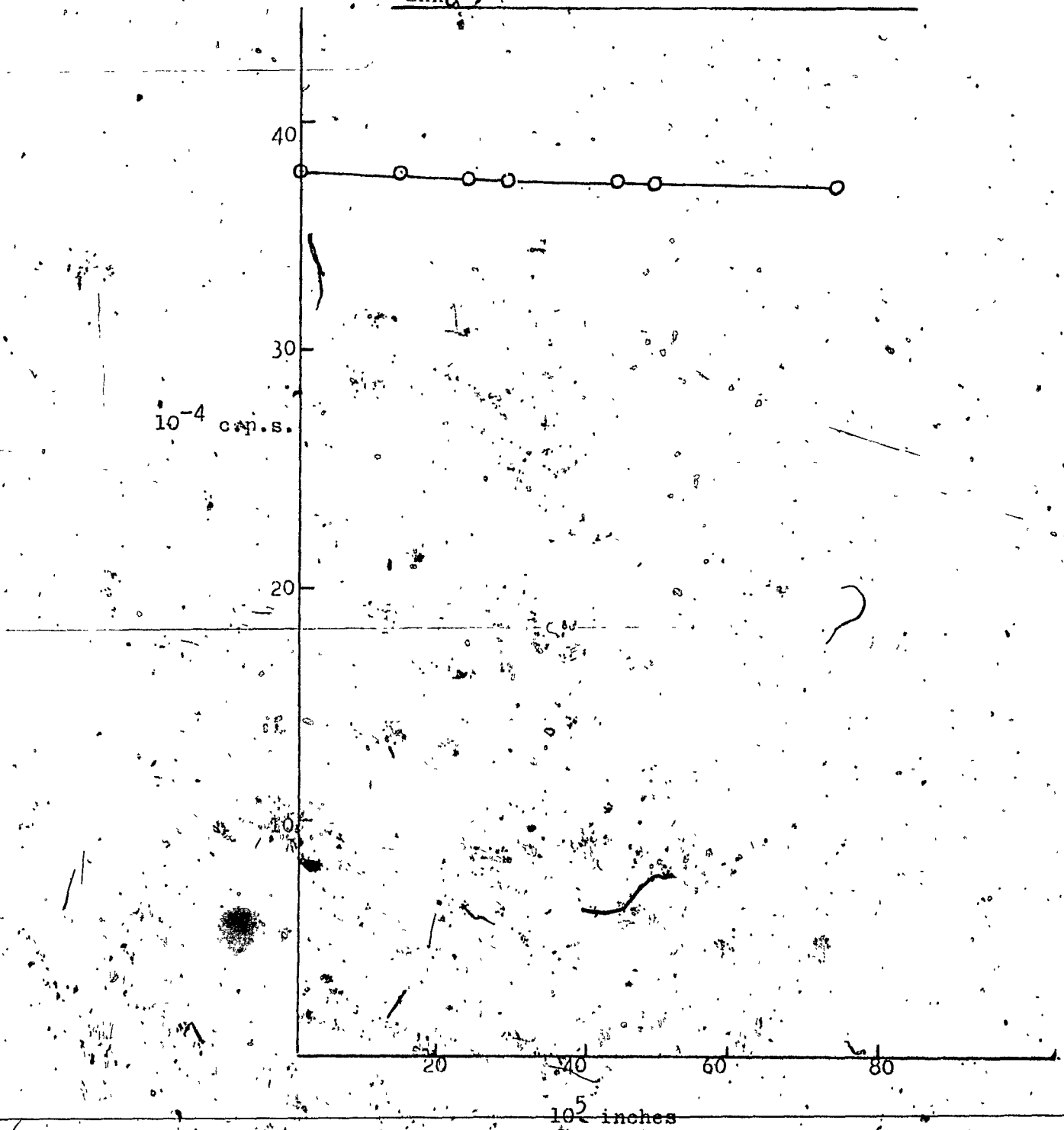


TABLE 4.1.17

ABSORPTIVE EFFECT OF MYLAR COVERING FOR AlK_α LINE IN LIQUID MEDIA WITH $C_{Al} = 0.035$

Thickness (10^5 inches)	* I_{AlK_α} (cps)	k
15	625	
25	363	0.12514
30	274	0.12640
45	129	0.12115
50	92	0.12585
75	21	0.13013

average k = 0.125^7

std. devn. = $\pm 0.003^2$

The intensity of uncovered specimen may be calculated by Equation (13), given as:-

$I^{corr.\ for\ mylar}_{AlK} = 1418$ cps

* counting time = 100 seconds

FIGURE 4.1.17

$I_{AlK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING

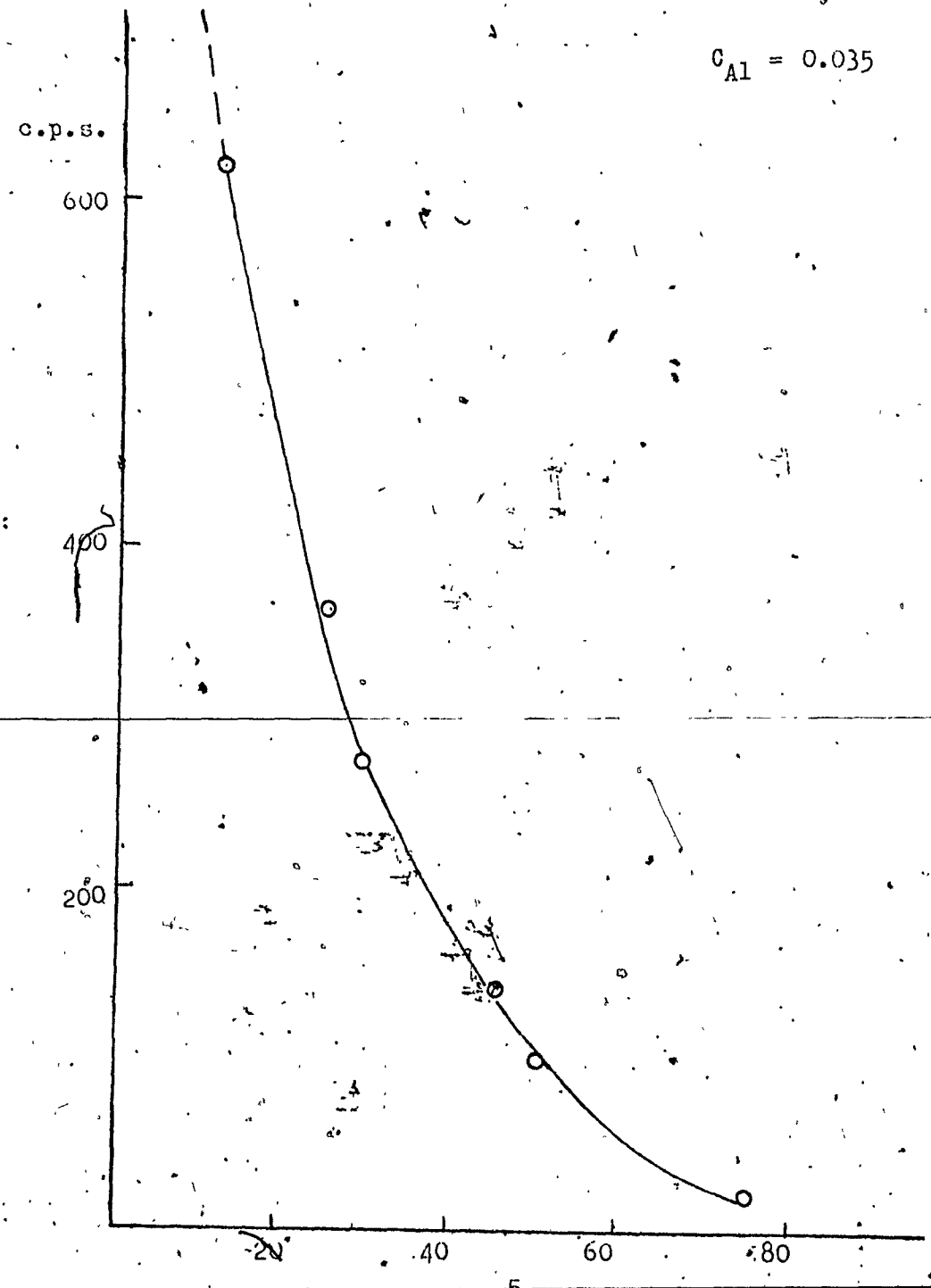


TABLE 4.1.18

ABSORPTIVE EFFECT OF MYLAR COVERING FOR AlK_α LINE IN LIQUID MEDIA WITH $C_{Al} = 0.025$

Thickness (10^5 inches)	*I_{AlK_α} (cps)	k
15	442	
25	254	0.12755
30	193	0.12719
45	85	0.12666
50	66	0.12837
75	15	0.12911

average $k = 0.1277^8$

std. devn. $= \pm 0.0003^0$

the intensity, of uncovered specimen may be calculated by Equation (13), is given as:-

$I^{Corr.\ for\ mylar}_{AlK} = 1011$ cps

* counting time = 100 seconds

FIGURE 4.1.18

I_{AlK_α} VERSUS THICKNESS OF MYLAR COVERING

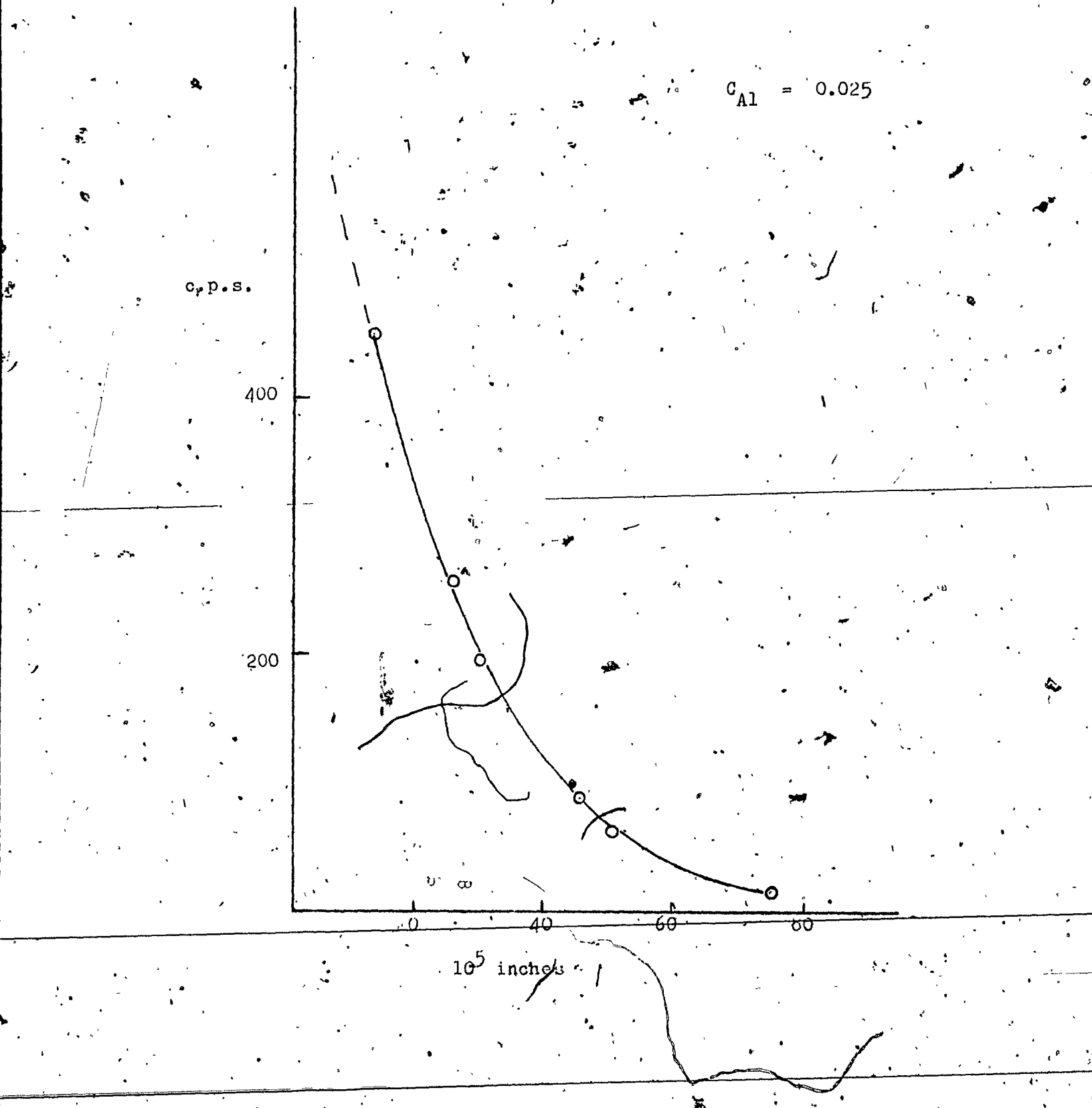


TABLE 4.1.1)

ABSORPTIVE EFFECT OF MYLAR COVERING FOR ClK_α LINE IN LIQUID MEDIA WITH $C_{Cl} = 0.04300$

Thickness (10^5 inches)	I_{ClK_α} (cps)	k
15	17726	
25	16210	0.02059
30	14877	0.02691
45	12774	0.02515
50	12179	0.02469
75	10231	0.02110

average $k = 0.023^7$

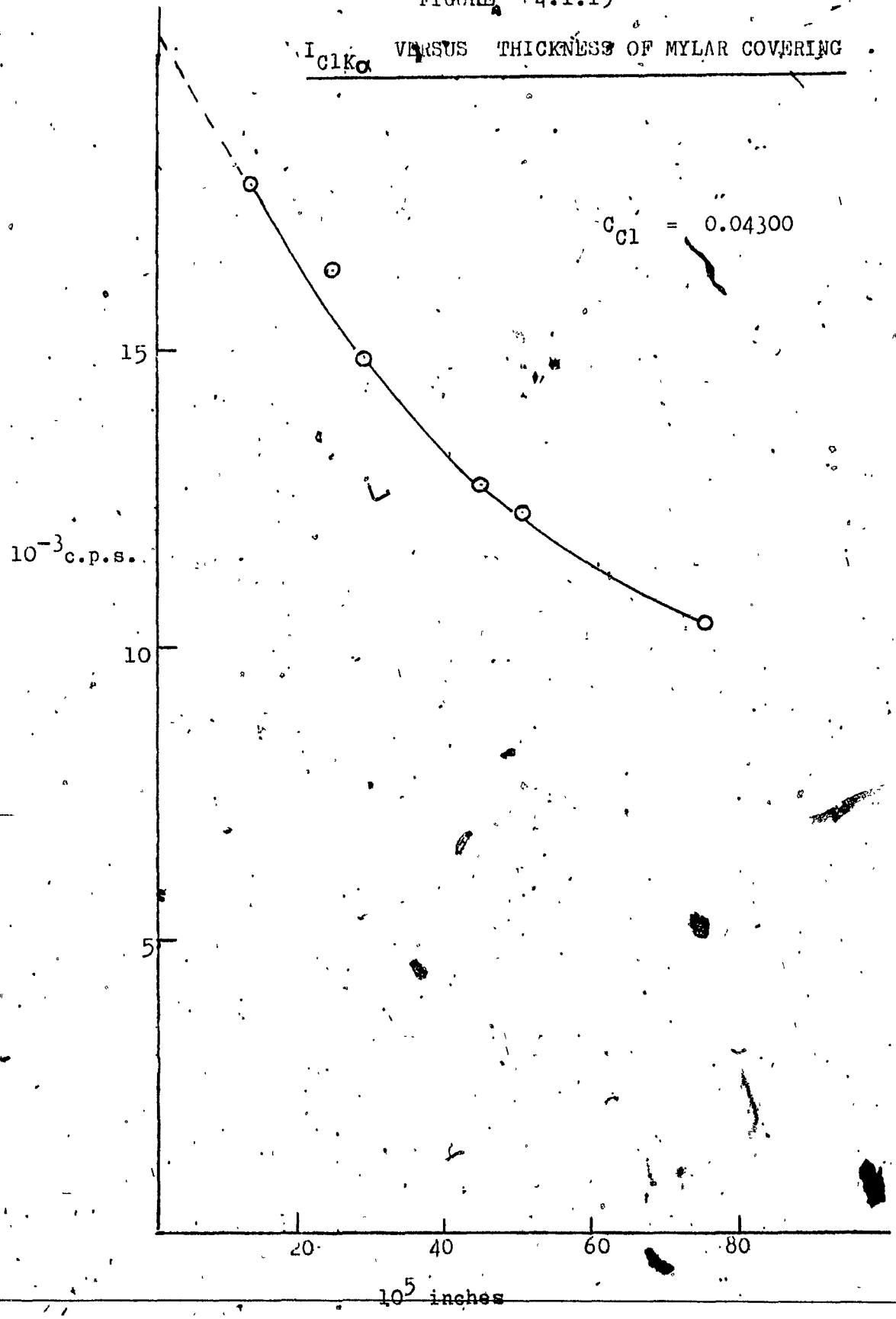
std. devn. $= \pm 0.002^7$

the intensity, of uncovered specimen may be calculated by Equation (13), is given:-

$$I_{ClK}^{\text{Corr. for mylar effect}} = 20683 \text{ cps}$$

FIGURE 4.1.19

$I_{ClK\alpha}$ VERSUS THICKNESS OF MYLAR COVERING



4.2 Interelement Effect

There are six sections to be presented:-

4.2.1 Effect on Al
4.2.2 Effect on Cl
4.2.3 Effect on Mn
4.2.4 Effect on Fe
4.2.5 Effect on Ni
4.2.6 Effect on Cu

Each section were shown in tables and figures:-

Tables involving "Parameter of XRF Analysis"

Tables involving "Solution Preparation" and "Intensity Measurement"

Solution preparation:-

Six or seven solutions of interest elements were prepared from the stock solutions which prepared previously. The concentration unit of each element or matrix was operated by weight fraction.

Intensity measurement:-

The measurement of intensity is expressed as the average of counts taken, and $I^{meas.}$ has been corrected by blank solution and/or background radiation, also deadtime correction may be required for $I^{meas.}$ previously. I^{My} was corrected by the mylar absorption.

Tables involving "Calculation of α-Correction Coefficients"

The values of α-correction coefficient may be determined

by using the Equation (17), (18) or (19)

$$\alpha_{AM} = \frac{I^{My}_{A(2)}C_{A(1)} - I^{My}_{A(1)}C_{A(2)}}{I^{My}_{A(1)}C_{A(2)}C_{M(1)} - I^{My}_{A(2)}C_{A(1)}C_{M(2)}} \quad (17)$$

$$\alpha_{AB} = \frac{(I^{My}_{A(2)}C_{A(1)} - I^{My}_{A(1)}C_{A(2)}) + \alpha_{AM}(I^{My}_{A(2)}C_{A(1)}C_{M(2)} - I^{My}_{A(1)}C_{A(2)}C_{M(1)})}{I^{My}_{A(1)}C_{A(2)}C_{B(1)} - I^{My}_{A(2)}C_{A(1)}C_{B(2)}} \quad (18)$$

$$\alpha_{AB} = \frac{I_{A(2)} - I_{A(1)} + \alpha_{AM}(I_{A(2)}C_{M(2)} - I_{A(1)}C_{M(1)})}{I_{A(1)}C_{B(1)} - I_{A(2)}C_{B(2)}} \quad (19)$$

where:-

M = $H_2O + HNO_3$ aqueous matrix

A, B = Al, Cl, Mn, Fe, Ni or Cu

The average value of α-correction coefficient was calculated and the standard deviation was also given.

Tables involving "Calculation of $I^{Corr.}$ and I^{o}"

The corrected intensity for M ($I^{Corr.\ for\ M}$) and the corrected

intensity for M and B ($I^{Corr.}$) of analyte of each solution which were both calculated by the use of the following equations:-

$$I_A^{Corr.\ for\ M} = I_A^{My} + \alpha_{AM} I_A^{My} C_M \qquad (20)$$

$$I_A^{Corr.} = I_A^{Corr.\ for\ M} + \alpha_{AB} I_A^{My} C_B \qquad (25)$$

The intensity of pure element I_A^o was calculated by Equation (21), and the average value of I_A^o and the standard deviation were also given.

$$I_A^o = \frac{I_A^{Corr.}}{C_A} \qquad (21)$$

Tables involving "Back Calculation"

Represent the back calculation of the analyte concentration:-

$$C_A^{Back} = \frac{I_A^{Corr.}}{I_A^o\ (average)} \qquad (22)$$

All C_A^{Back} values calculated to same significant figure position as C_A (known).

The absolute and relative percent error were also given

$$\text{Absolute error} = \left| C_A^{Back} - C_A \right| \qquad (23)$$

$$\% \text{ error} = (\text{Absolute error})/C_A \qquad (24)$$

Figures represent the "Spectrometer Scan" of AlKα and ClKα

Which gave the informations:-

(1) 2θ and background angles chosen

(2) net intensity measurement

Figures involving " I_A Versus C_B, C_M, etc"

$I_A^{meas.}$, I_A^{My}, $I_A^{Corr.\ for\ M}$ and $I_A^{Corr.}$ versus the concentration of M (C_M) and effected elements (C_{Al}, C_{Cl}, C_{Mn}, etc) were plotted on this figure and the circles surrounding each experimentally determined locus on a curve are for identification of the locus only, they do not reflect the uncertainty parameters around the locus.

4.2.1 EFFECT ON Al

INSTRUMENT PARAMETERS

TUBE TARGET	Cr
kV	50
mA	36
COUNTER	PF
COLLIMATOR	COARSE
HELIUM FLOW	5 c.f.h.
P10 FLOW	0.1 c.f.h.
CRYSTAL	PET
HIGH VOLTAGE DETECTOR	3.50 HELIPOT
GAIN	10
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	145.17
2θ Background	147.50
ω	0.16
COUNTING TIME	50 sec.

4.2.1.1 SYSTEM Al - M

(a)

Solution	C_{Al}	C_M	$I^{meas}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
A-1	0.01000	0.99000	101	398
A-2	0.01500	0.98500	152	599
A-3	0.02000	0.98000	203	801
A-4	0.02500	0.97500	255	1004
A-5	0.03000	0.97000	307	1208
A-6	0.03500	0.96500	359	1414
A-7	0.03708	0.96292	381	1499

(b)

	α_{AlM}
Solution A-1/Solution A-7	1.18191
" A-1/ " A-6	1.16261
" A-1/ " A-5	1.13247
" A-1/ " A-4	1.18071
" A-2/ " A-7	1.38543
" A-2/ " A-6	1.37954
" A-2/ " A-5	1.41124
" A-3/ " A-7	1.39017
" A-3/ " A-6	1.38310
" A-4/ " A-7	1.18317

average $\alpha_{AlM} = 1.2^8$

std. devn. $\sigma = \pm 0.1^2$

(c)

Solution	C_{Al}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
A-1	0.01000	0.99000	398	903	00325
A-2	0.01500	0.98500	599	1354	00236
A-3	0.02000	0.98000	801	1805	00244
A-4	0.02500	0.97500	1004	2257	00296
A-5	0.03000	0.97000	1208	2708	00269
A-6	0.03500	0.96500	1414	3159	00270
A-7	0.03708	0.96292	1499	3347	00270

average $I^{o}_{AlK\alpha}$ = 00270 cps

std. devn. = ± 30 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$ (cps)	C^{Back}_{Al}	Absolute error	% error
A-1	0.01000	903	0.0100	0.00000	0.0
A-2	0.01500	1354	0.01500	0.00000	0.0
A-3	0.02000	1805	0.02000	0.00000	0.0
A-4	0.02500	2257	0.02500	0.00000	0.0
A-5	0.03000	2708	0.03000	0.00000	0.0
A-6	0.03500	3159	0.03500	0.00000	0.0
A-7	0.03708	3347	0.03708	0.00000	0.0

FIGURE 4.2.1.1.1 (AlKα)

Sample: 1/ C_{Al} = 0.035 in aqueous
2/ Blank = H_2O + HNO_3 aqueous

Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} - I_1^{2\theta Bkg}) - (I_2^{2\theta} - I_2^{2\theta Bkg})$

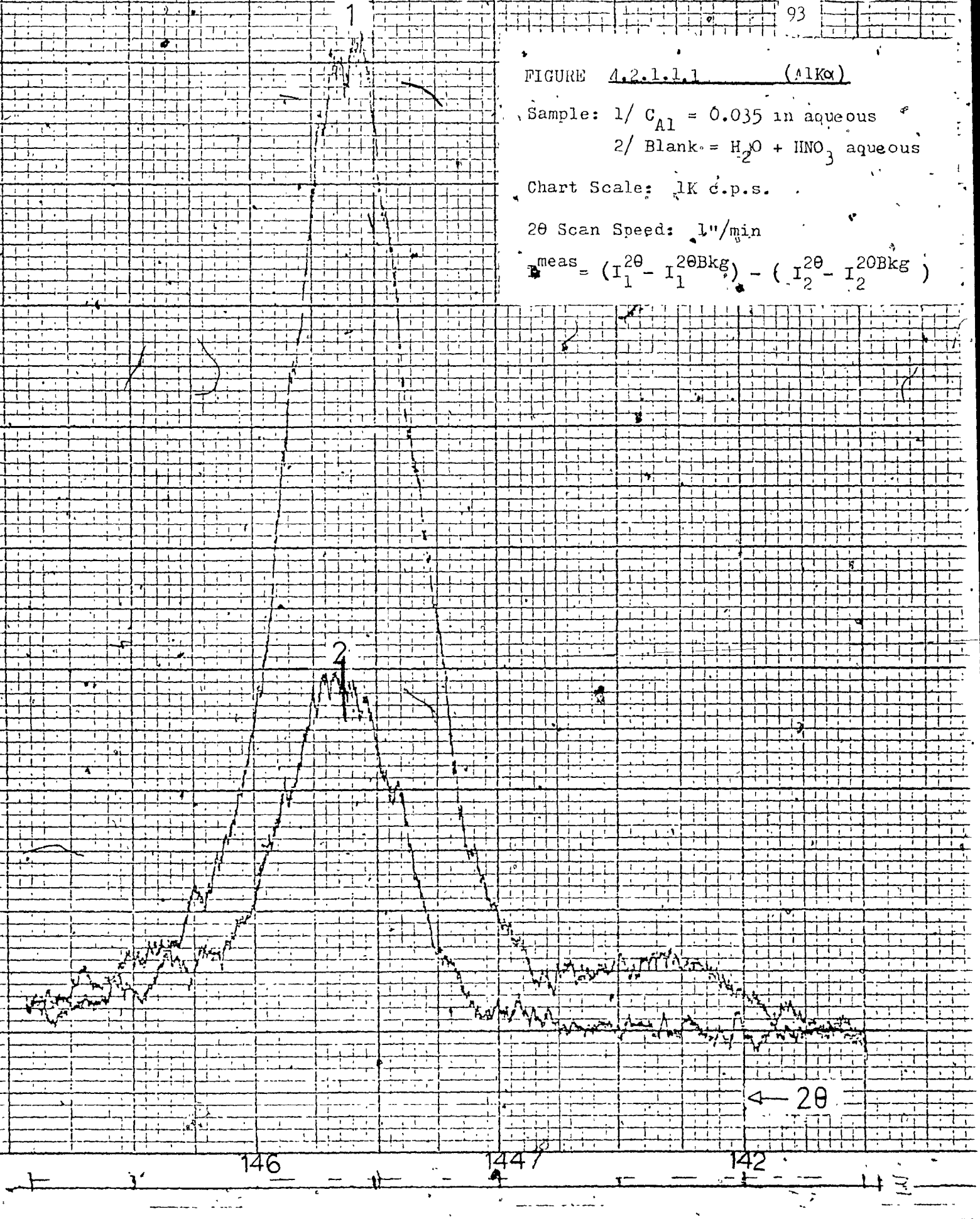
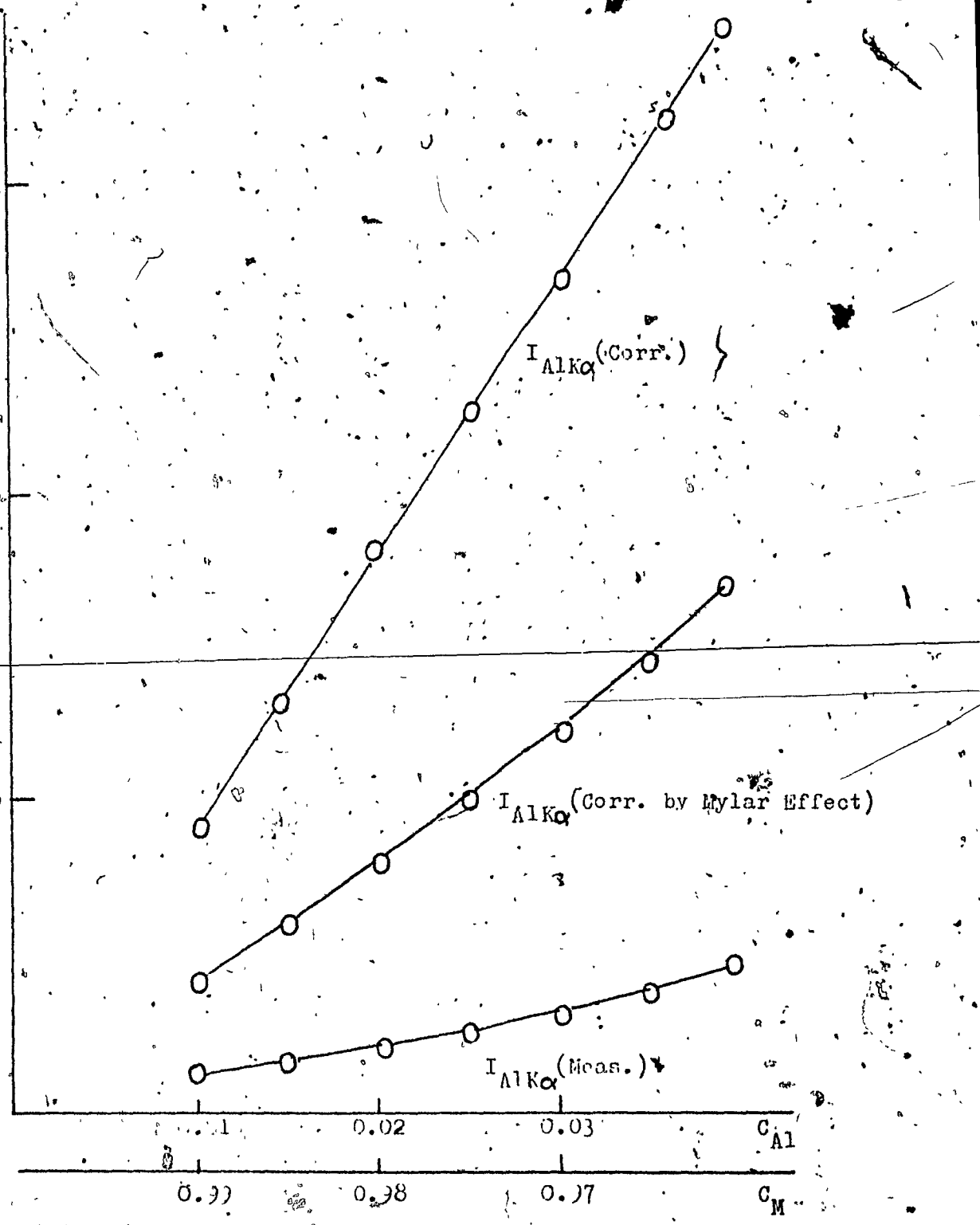


FIGURE 4.2.1.1.

$I_{AlK\alpha}$ VERSUS C_{Al} AND C_M



4.2.1.2 EFFECT OF Cl ADDITION ON Al

(a)

Solution	C_{Al}	C_{Cl}	C_M	$I^{meas.}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
ACl-1	0.02000	0.00000	0.98000	215	844
ACl-2	0.02000	0.01156	0.96842	213	840
ACl-3	0.02000	0.03237	0.94763	213	837
ACl-4	0.02000	0.04316	0.93684	212	834
ACl-5	0.02000	0.05395	0.92605	211	831
ACl-6	0.02000	0.06474	0.91526	211	829
ACl-7	0.02000	0.08632	0.89368	209	824

(b)

	α_{AlCl}
Solution ACl-1/Solution ACl-7	1.03690
" 1 " 6	1.03474
" 1 " 5	1.03251
" 1 " 4	1.02818
" 2 " 7	1.03072
" " " 6	1.03262
" 2 " 5	2.02528
" 3 " 7	1.01171
" 3 " 6	1.01063
" 4 " 7	1.02459

average α_{AlCl} = 1.03^3

std. devn. = $\pm 0.03^3$

(c)

Solution	C_{Al}	C_{Cl}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{Corr.}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
ACl-1	0.02000	0.00000	0.98000	844	1904	1904	95180
ACl-2	0.02000	0.02158	0.95842	840	1870	1905	95250
ACl-3	0.02000	0.03237	0.94763	837	1851	1904	95180
ACl-4	0.02000	0.04316	0.93684	834	1834	1904	95200
ACl-5	0.02000	0.05395	0.92605	831	1816	1903	95134
ACl-6	0.02000	0.06474	0.91526	829	1800	1904	95224
ACl-7	0.02000	0.08632	0.89368	824	1767	1905	95240

average $I^{o}_{AlK\alpha}$ = 95200 cps

std. devn. = ± 400 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$	C^{Back}_{Al}	Absolute error	% error
ACl-1	0.02000	1904	0.02000	0.00000	0.00
ACl-2	0.02000	1905	0.02001	0.00001	0.05
ACl-3	0.02000	1904	0.02000	0.00000	0.00
ACl-4	0.02000	1904	0.02000	0.00000	0.00
ACl-5	0.02000	1903	0.01999	0.00001	0.05
ACl-6	0.02000	1904	0.02000	0.00000	0.00
ACl-7	0.02000	1905	0.02001	0.00001	0.05

PICTURE 4...1.2.1 ($AlK\alpha$)

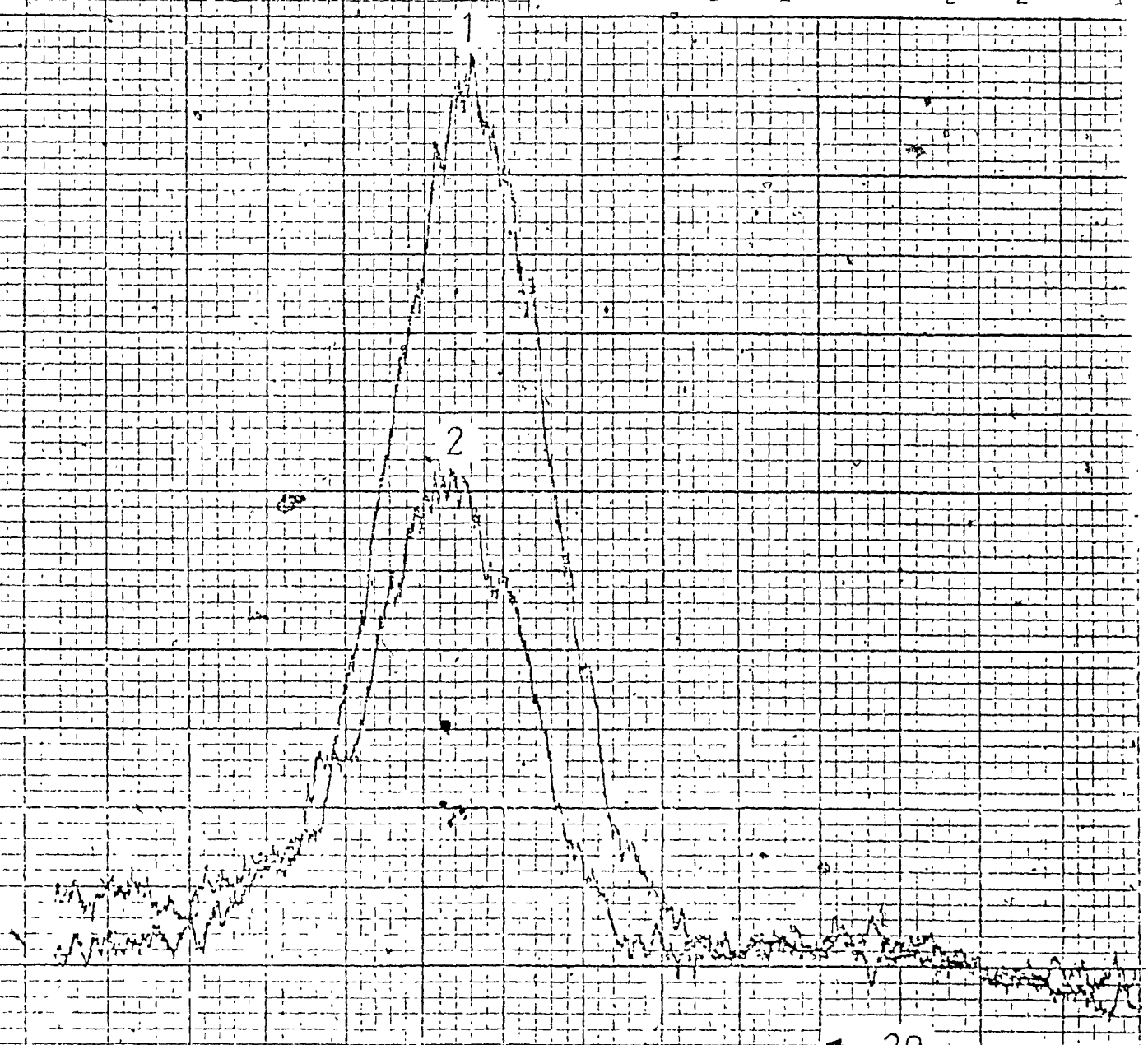
Sample: 1/ $C_{Al} = 0.02$ in aqueous
$C_{Cl} = 0.064743$

2/ $C_{Cl} = 0.064743$ in aqueous

Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} - I_1^{2\theta Bkg}) - (I_2^{2\theta} - I_2^{2\theta Bkg})$



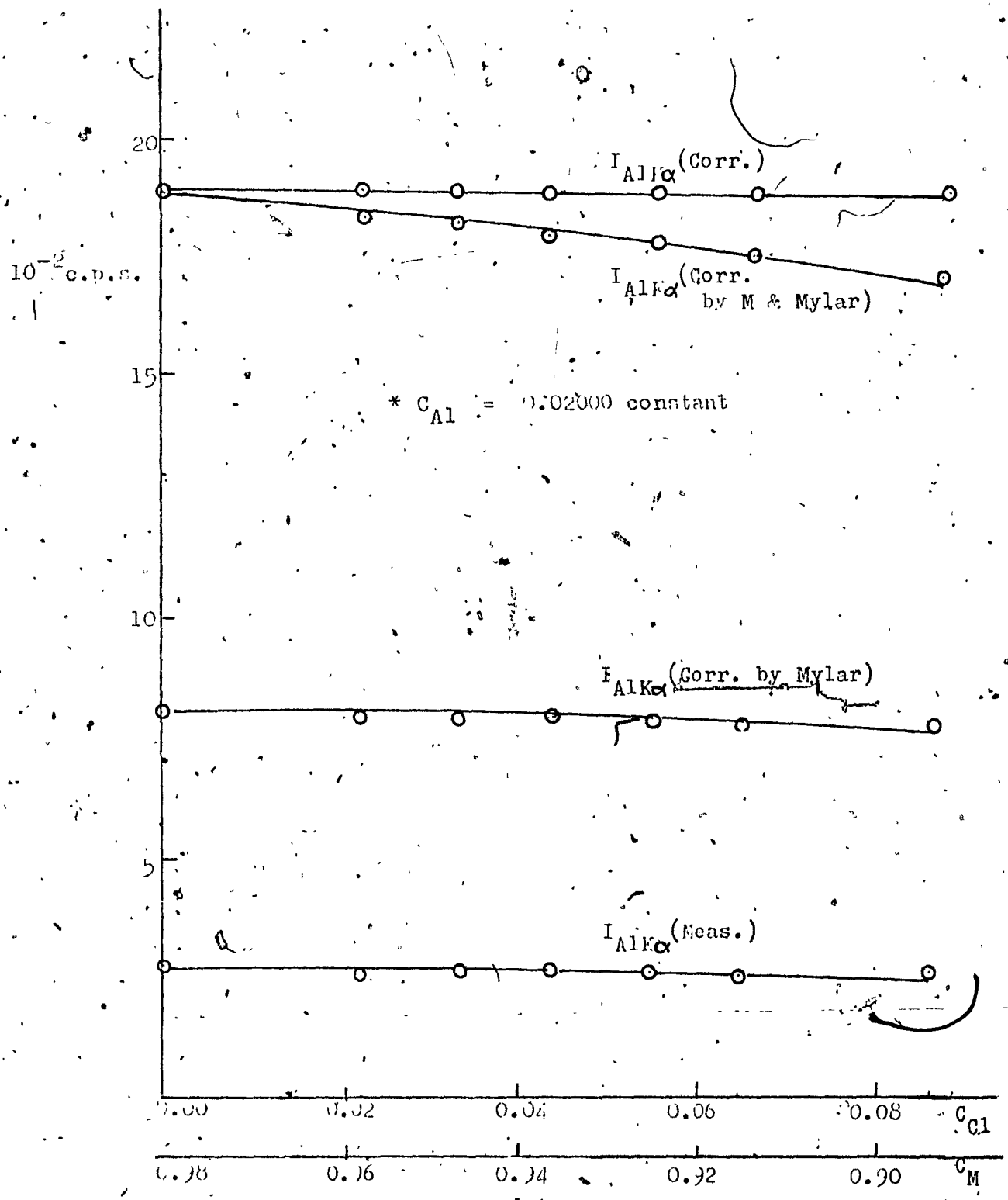
146 144 142

CHART NO. WH

CHART NO.

FIGURE 4.2.1.2.2

$I_{AlK\alpha}$ VERSUS C_{Cl} AND C_M



4.2.1.3 EFFECT OF Mn AND F ON Al

(a)

Solution	C_{Al}	C_{Mn}	C_{F}	$I^{meas.}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
AM-1	0.02000	0.00000	0.98000	178	700
AM-2	0.02000	0.01500	0.96500	176	694
AM-3	0.02000	0.02000	0.96000	175	690
AM-4	0.02000	0.02500	0.95500	174	685
AM-5	0.02000	0.03000	0.95000	173	681
AM-6	0.01015	0.03830	0.94255	165	650

(b)

	α_{AlMn}	
Solution AM-1/Solution AM-6	3.08334	
" 1 " 5	3.48971	
" 1 " 4	3.30761	
" 2 " 6	4.17092	(reject)
" 2 " 5	4.11317	(reject)
" 3 " 6	3.29494	

average α_{AlMn} = 3.2^{7}

std. devn. = $\pm 0.3^{0}$

(c)

Solution	C_{Al}	C_{Mn}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{Corr}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
AM-1	0.02000	0.00000	0.98000	700	1579	1579	78938
AM-2	0.02000	0.01500	0.96500	694	1550	1584	79216
AM-3	0.02000	0.02000	0.96000	690	1539	1584	79198
AM-4	0.02000	0.02500	0.95500	685	1542	1578	78904
AM-5	0.02000	0.03000	0.95000	681	1509	1576	79182
AM-6	0.01915	0.03830	0.94255	650	1435	1516	79182

average, $I^{o}_{AlK\alpha}$ = 79000 cps

std. devn. = ± 200 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$ (cps)	C^{Back}_{Al}	Absolute error	% error
AM-1	0.02000	1579	0.01998	0.00002	0.1
AM-2	0.02000	1584	0.02004	0.00004	0.20
AM-3	0.02000	1584	0.02004	0.00004	0.20
AM-4	0.02000	1578	0.01996	0.00004	0.20
AM-5	0.02000	1576	0.01994	0.00006	0.30
AM-6	0.01915	1516	0.01918	0.00003	0.16

Figure 4.2.1.3.1 (AlKα)

Sample: 1/ C_{Al}=0.02 C_{Mn}=0.015 in aqueous

2/ C_{Mn}=0.015 in aqueous

Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} - I_1^{2\theta Bkg}) - (I_2^{2\theta} - I_2^{2\theta Bkg})$

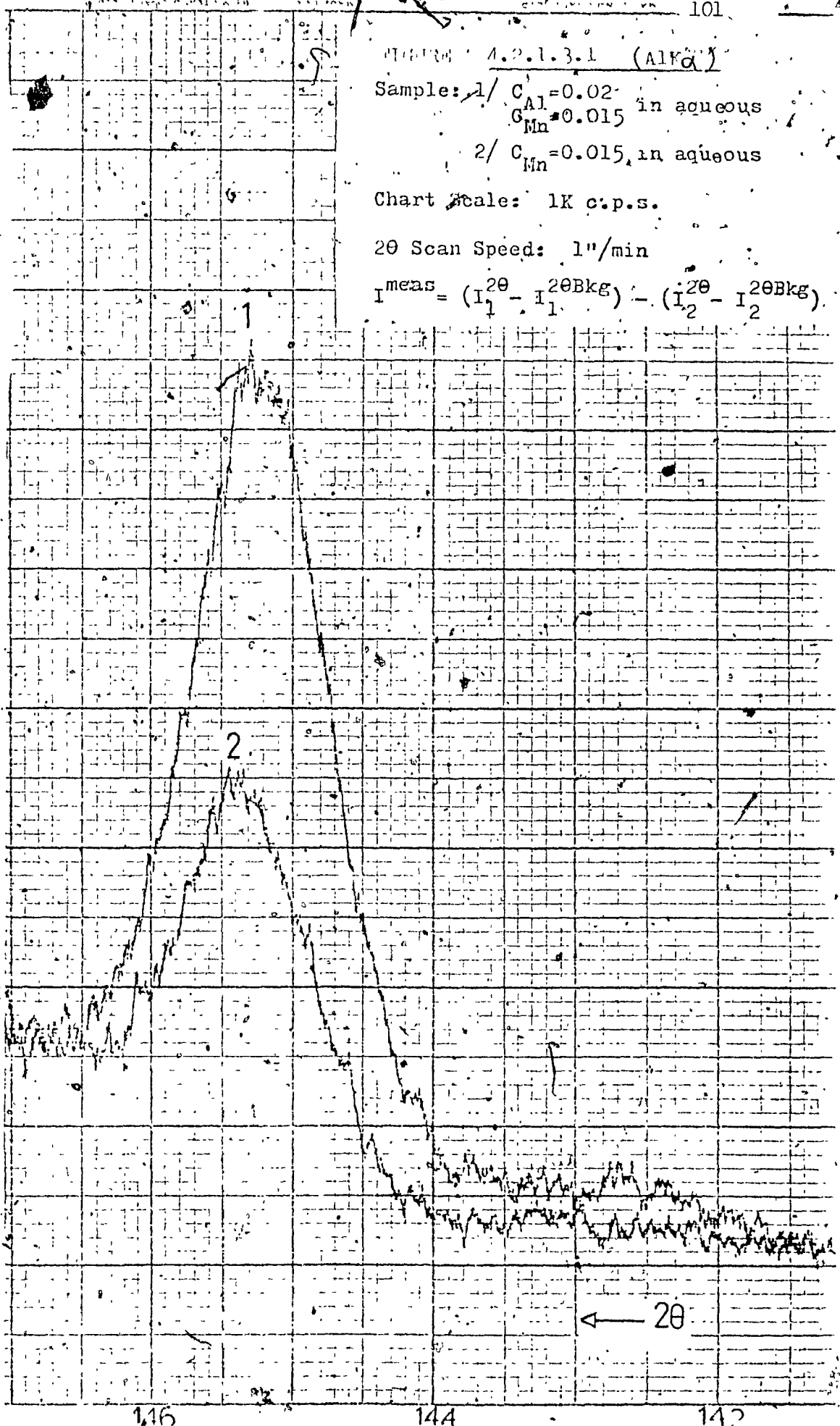
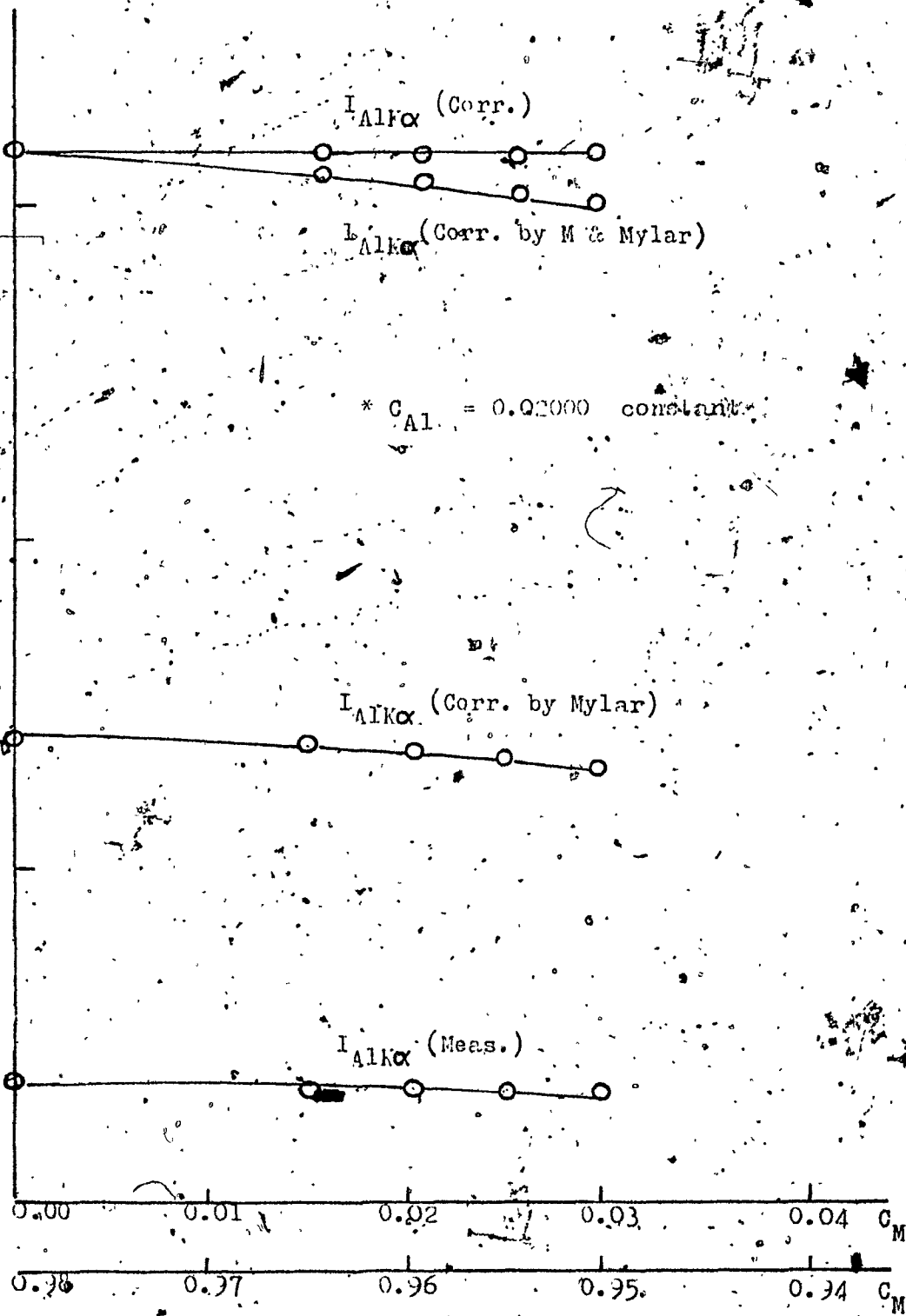


FIGURE 4.2.1.3.2

$I_{AlK\alpha}$ VERSUS C_{Mn} AND C_M



4.2.1.4 EFFECT OF Fe AND M ON Al

(a).

Solution	C_{Al}	C_{Fe}	C_M	$I^{meas}_{AlK\alpha}$(cps)	$I^{My}_{AlK\alpha}$(cps)
AF-1	0.02000	0.00000	0.98000	190	747
AF-2	0.02000	0.01000	0.97000	186	733
AF-3	0.02000	0.01500	0.96500	185	727
AF-4	0.02000	0.02000	0.96000	183	722
AF-5	0.02000	0.02500	0.95500	182	716
AF-6	0.02000	0.03000	0.95000	180	710
AF-7	0.01798	0.03596	0.94606	160	628

(b)

	α_{AlFe}
Solution AF-1/Solution AF-7	5.56487
" 1 " 6	4.08881
" 1 " 5	5.21000
" 1 " 4	5.24714
" 2 " 7	5.53524
" 2 " 6	4.74444
" 2 " 5	5.01474
" 3 " 7	5.58271
" 3 " 6	4.66762
" 3 " 7	5.06779

average α_{AlFe} = 5.26

std. devn. = ± 0.36

(c)

Solution	C_{Al}	C_{Fe}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I_{AlK\alpha}$ Corr. for M (cps)	$I_{AlK\alpha}$ Corr. (cps)	$I^{o}_{AlK\alpha}$ (cps)
AF-1	0.02000	0.00000	0.98000	747	1684	1684	84213
AF-2	0.02000	0.01000	0.97000	733	1644	1683	84129
AF-3	0.02000	0.01500	0.96500	727	1624	1681	84061
AF-4	0.02000	0.02000	0.96000	722	1609	1684	84220
AF-5	0.02000	0.02500	0.95500	716	1591	1685	84257
AF-6	0.02000	0.03000	0.95000	710	1573	1684	84223
AF-7	0.01798	0.03596	0.94606	628	1389	1507	83831

average $I^{o}_{AlK\alpha}$ = 84100 cps

std. devn. = ± 200 cps

(d)

Solution	C_{Al}	$I_{AlK\alpha}$ Corr.	C^{Back}_{Al}	Absolute error	% error
AF-1	0.02000	1684	0.02002	0.00002	0.10
AF-2	0.02000	1683	0.02000	0.00000	0.00
AF-3	0.02000	1681	0.01998	0.00002	0.10
AF-4	0.02000	1684	0.02002	0.00002	0.10
AF-5	0.02000	1685	0.02003	0.00003	0.15
AF-6	0.02000	1684	0.02004	0.00004	0.20
AF-7	0.01798	1507	0.01791	0.00007	0.40

FIGURE 4.2.1.4.1 ($AlK\alpha$)

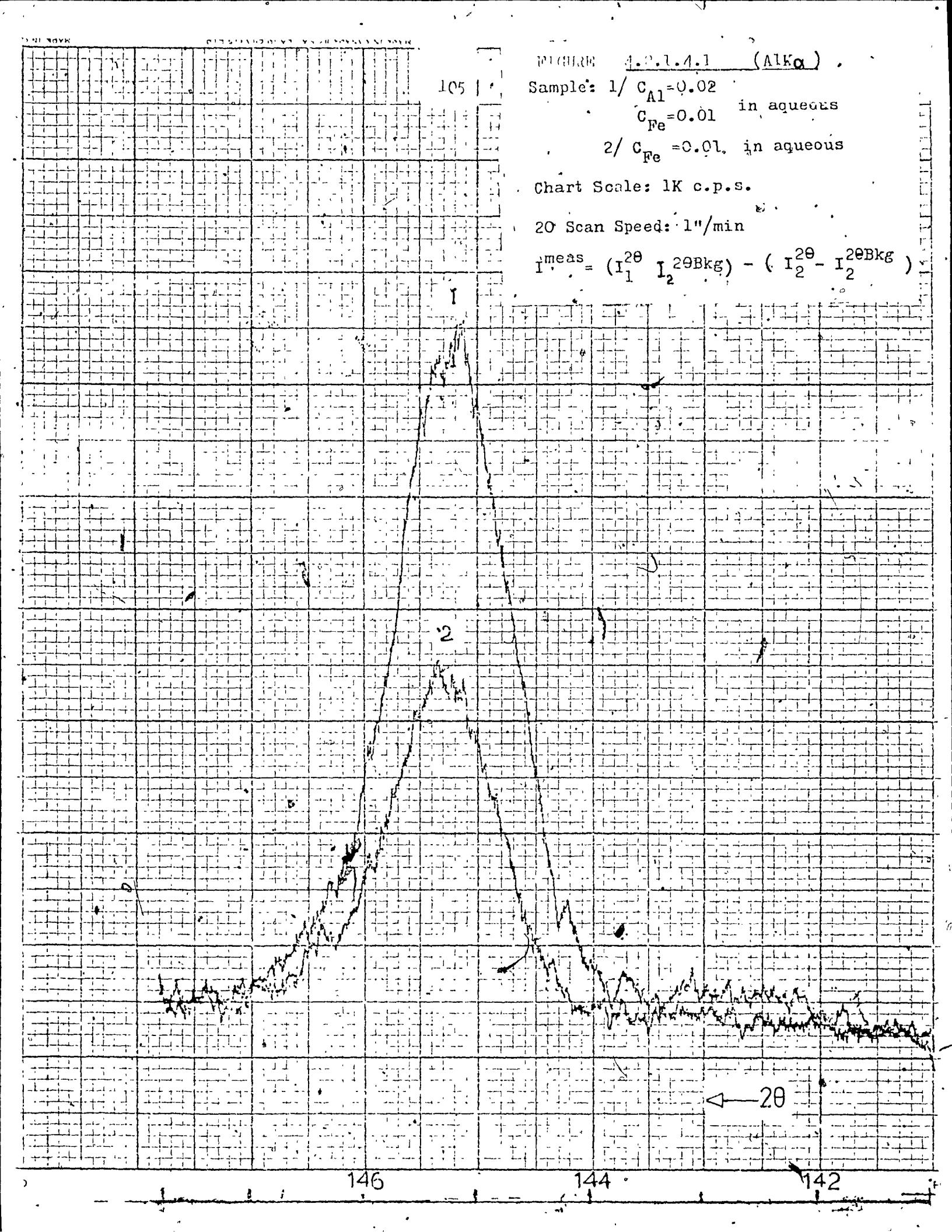
Sample: 1/ C_{Al}=0.02
C_{Fe}=0.01 in aqueous

2/ C_{Fe} =0.01 in aqueous

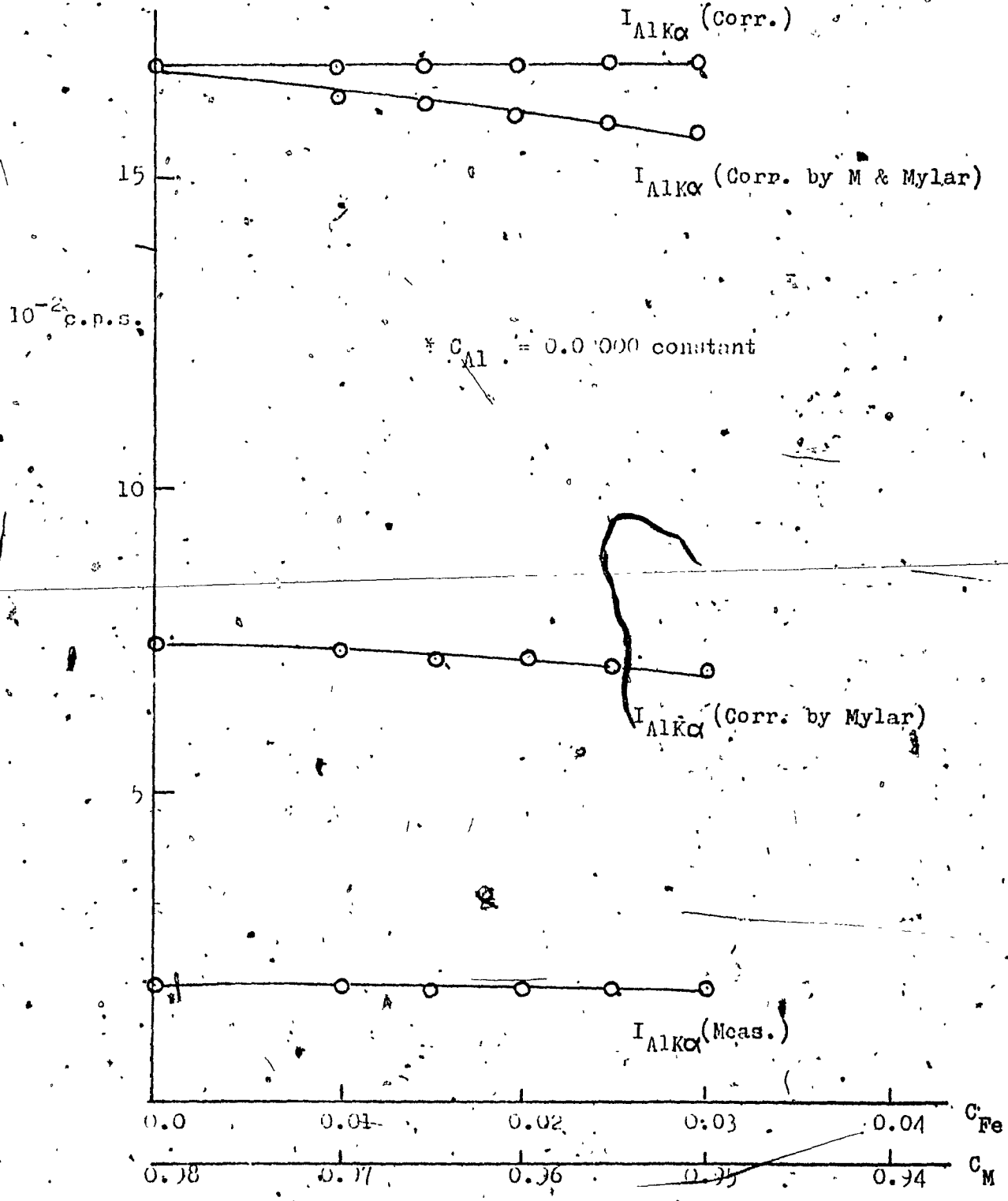
Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} I_2^{2\theta Bkg}) - (I_2^{2\theta} - I_2^{2\theta Bkg})$



$I_{AlK\alpha}$ VERSUS C_{Fe} AND C_M



4.4.1.5. EFFECT OF Ni AND Fe ON Al

(a)

Solution	C_{Al}	C_{Ni}	C_{Fe}	$I^{meas.}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
AN-1	0.03000	0.00000	0.00000	[illegible]	833
AN-2	0.03000	0.01000	0.07000	1206	812
AN-3	0.03000	0.01500	0.06500	1204	801
AN-4	0.03000	0.02000	0.06000	1203	792
AN-5	0.03000	0.02500	0.05500	1196	781
AN-6	0.03000	0.03000	0.05000	1176	772
AN-7	0.03000	0.03771	0.04348	1160	710

(b)

	α_{AlNi}
Solution AN-1 / Solution AN-7	7.12742
" 1 " 6	7.16477
" 1 " 5	7.32541
" 1 " 4	7.14668
" 2 " 7	7.16704
" 2 " 6	7.24262
" 2 " 5	7.53374
" 3 " 7	7.08708
" 3 " 6	7.16473
" 4 " 7	7.10372

average α_{AlNi} = 7.21

std. devn. = ± 0.13

(c)

Solution	C_{Al}	C_{Ni}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{Corr.}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
AN-1	0.02000	0.00000	0.98000	833	1878	1878	93875
AN-2	0.02000	0.01000	0.97000	812	1820	1879	94948
AN-3	0.02000	0.01500	0.96500	801	1791	1878	93898
AN-4	0.02000	0.02000	0.96000	792	1764	1878	93907
AN-5	0.02000	0.02500	0.95500	781	1735	1875	93764
AN-6	0.02000	0.03000	0.95000	772	1711	1878	93922
AN-7	0.01871	0.03741	0.94388	710	1567	1758	93988

average $I^{o}_{AlK\alpha}$ = 93900 cps

std. devn. = ± 70 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$	C^{Back}_{Al}	Absolute error	% error
AN-1	0.02000	1878	0.02000	0.00000	0.00
AN-2	0.02000	1879	0.02001	0.00001	0.05
AN-3	0.02000	1878	0.02000	0.00000	0.00
AN-4	0.02000	1878	0.02000	0.00000	0.00
AN-5	0.02000	1875	0.01997	0.00003	0.16
AN-6	0.02000	1878	0.02000	0.00000	0.00
AN-7	0.01871	1758	0.01872	0.00001	0.06

FIGURE 4.2.1.5.1 (Alla)

Sample: 1/ C_{Al} = 0.02
C_{Ni} = 0.01 in aqueous
2/ C_{Ni} = 0.01 in aqueous

Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} - I_1^{2\theta Bkg}) - (I_2^{2\theta} - I_2^{2\theta Bkg})$

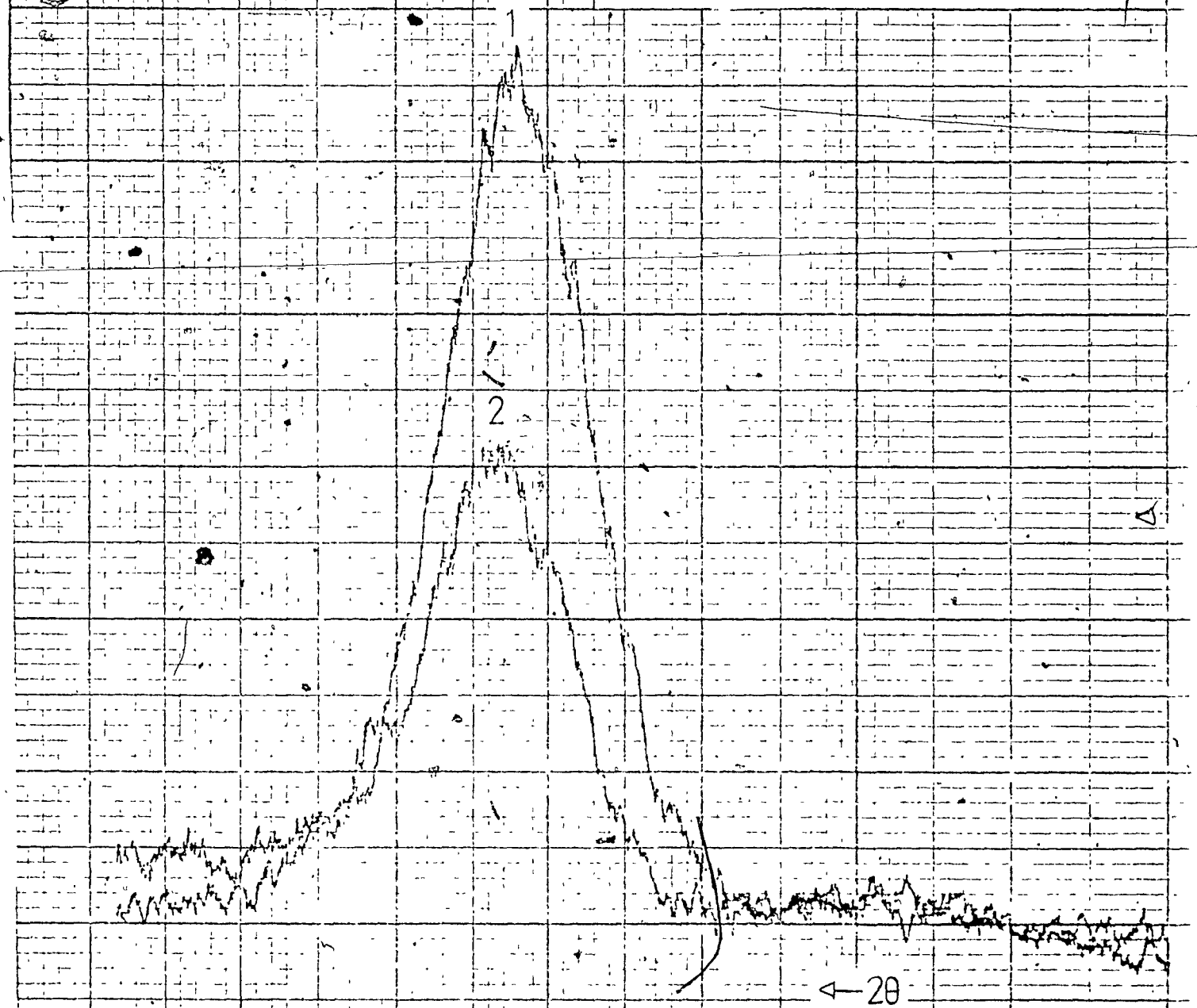
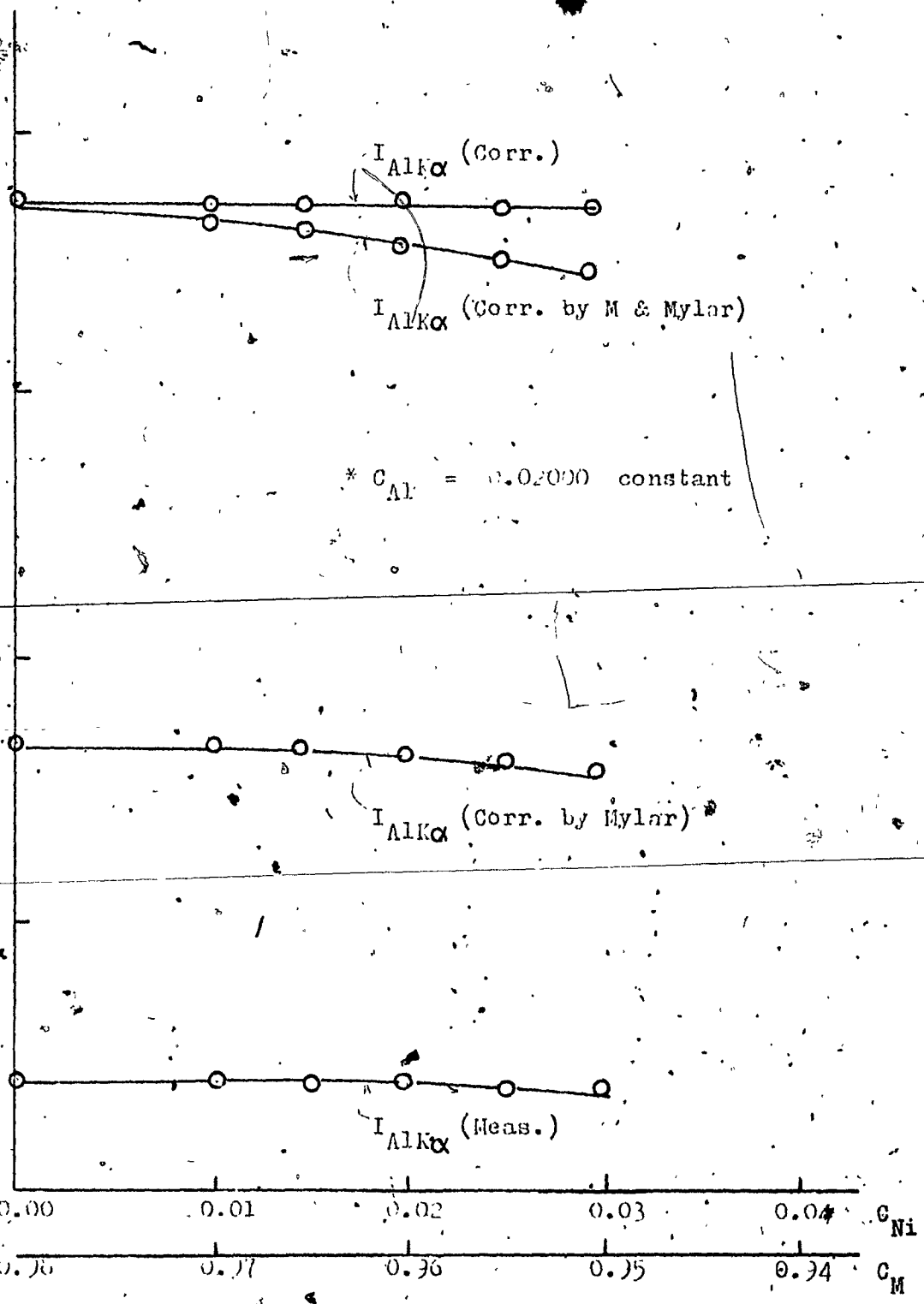


FIGURE [illegible]

$I_{AlK\alpha}$ VERSUS C_{Ni} AND C_M



4.2.1.6 EFFECT OF Cu AND M^{9} ON Al

(a)

Solution	C_{Al}	C_{Cu}	C_{M}	$I^{meas}_{AlK\alpha}$ (cps)	$I^{My}_{AlK\alpha}$ (cps)
AC-1	0.02500	0.00000	0.97500	210	825
AC-2	0.02500	0.01000	0.96500	204	803
AC-3	0.02500	0.02000	0.95500	199	781
AC-4	0.02500	0.04000	0.93500	190	747
AC-5	0.02500	0.05000	0.92500	183	722
AC-6	0.02500	0.06000	0.91500	180	707
AC-7	0.02276	0.06821	0.90903	161	634

(b)

	α_{AlCu}
Solution AC-1/Solution AC-7	7.31794
" 1 " 6	7.50855
" 1 " 5	7.72956
" 1 " 4	7.17321
" 2 " 7	7.26996
" 2 " 6	7.49795
" 2 " 5	7.77079
" 3 " 7	7.20340
" 3 " 6	7.48346
" 4 " 7	7.56300

average α_{AlCu} = 7.4^{b}

std. devn. = $\pm$ 0.2^{1}

(c)

Solution	C_{Al}	C_{Cu}	C_M	$I^{My}_{AlK\alpha}$ (cps)	$I^{Corr.\ for\ M}_{AlK\alpha}$ (cps)	$I^{Corr.}_{AlK\alpha}$ (cps)	$I^{o}_{AlK\alpha}$ (cps)
AC-1	0.02500	0.00000	0.97500	825	1855	1855	74184
AC-2	0.02500	0.01000	0.96500	803	1794	1854	74152
AC-3	0.02500	0.02000	0.95500	781	1737	1853	74121
AC-4	0.02500	0.04000	0.93500	747	1640	1863	74517
AC-5	0.02500	0.05000	0.92500	723	1576	1845	73782
AC-6	0.02500	0.06000	0.91500	707	1536	1852	74084
AC-7	0.02266	0.06821	0.90903	634	1372	1694	74434

average $I^{o}_{AlK\alpha}$ = 74200 cps

std. devn. = ± 200 cps

(d)

Solution	C_{Al}	$I^{Corr.}_{AlK\alpha}$ (cps)	C^{Back}_{Al}	Absolute error	% error
AC-1	0.02500	1855	0.02502	0.00002	0.08
AC-2	0.02500	1854	0.02499	0.00001	0.04
AC-3	0.02500	1853	0.02498	0.00002	0.08
AC-4	0.02500	1863	0.02511	0.00011	0.44
AC-5	0.02500	1845	0.02487	0.00013	0.52
AC-6	0.02500	1852	0.02497	0.00003	0.14
AC-7	0.02276	1694	0.02284	0.00008	0.35

Figure 4.2.1.6.1 ($AlK\alpha$)

Sample: 1/ $C_{Al} = 0.02$
$C_{Cu} = 0.01$ in aqueous

2/ $C_{Cu} = 0.01$ in aqueous

Chart Scale: 1K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = (I_1^{2\theta} - I_1^{2\theta Bkg}) - \gamma(I_2^{2\theta} - I_2^{2\theta Bkg})$

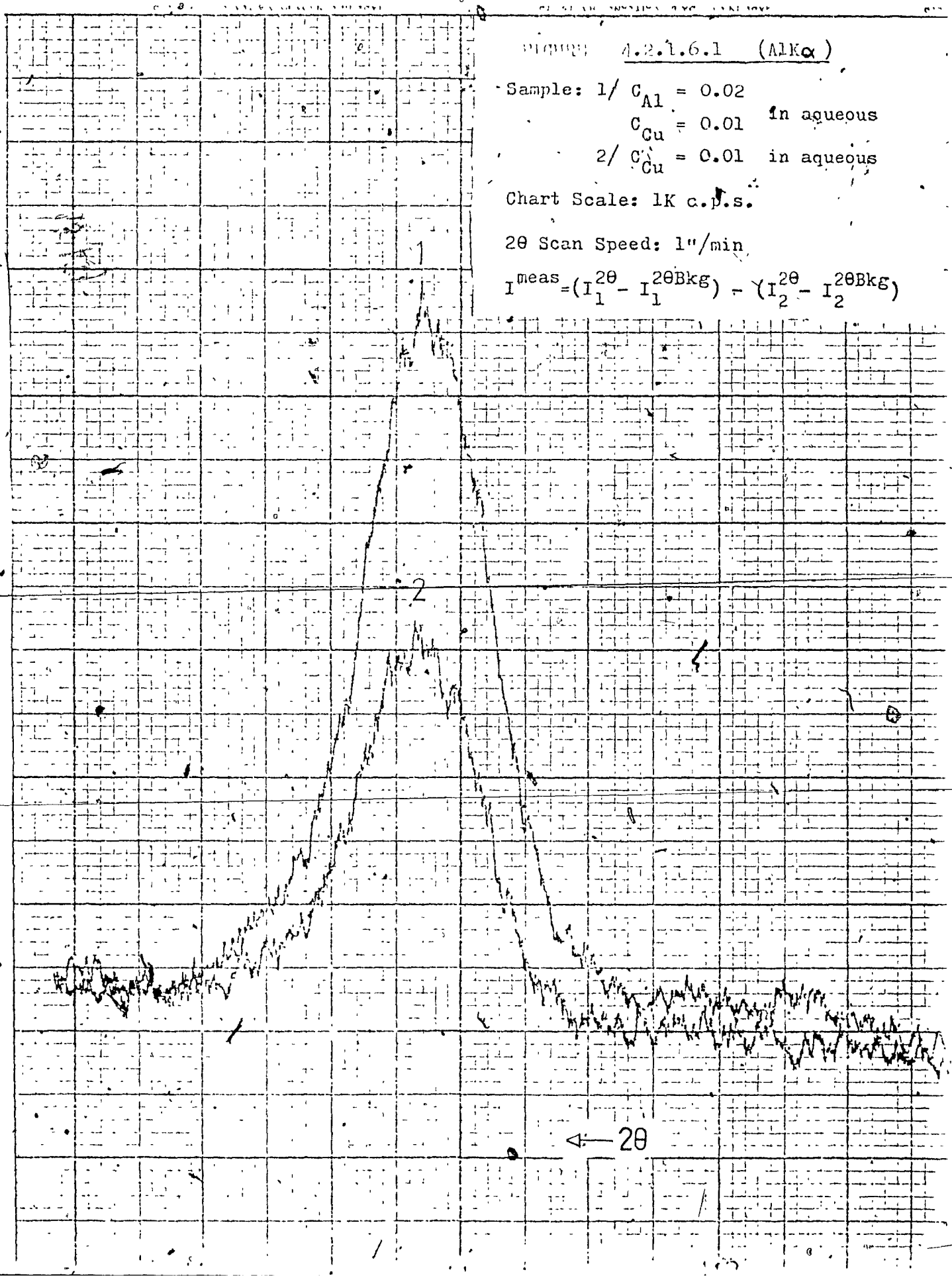
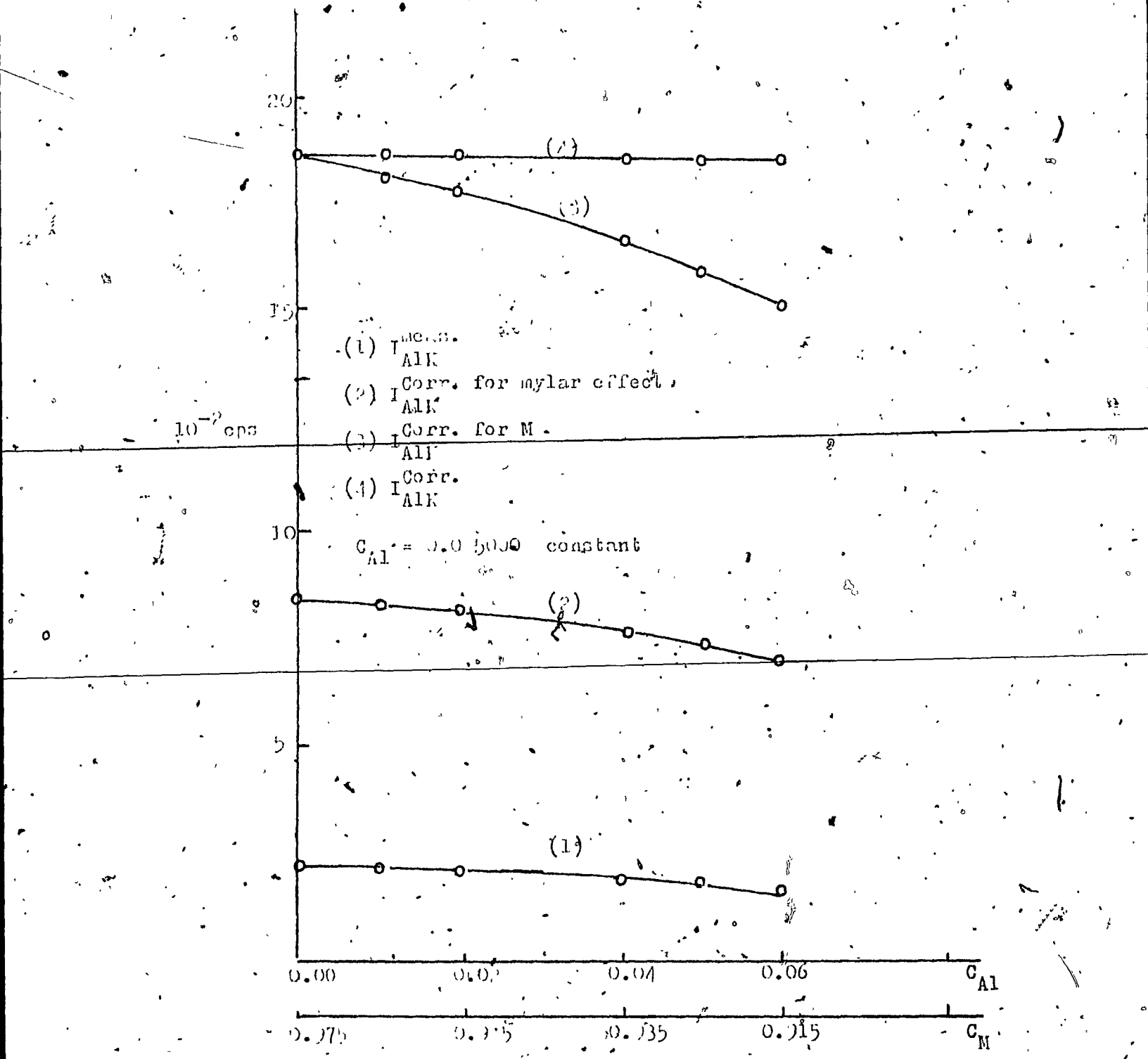


FIGURE A.2.1.6.2

$I_{Al\,K\alpha}$ VERSUS C_{Cu} AND C_M



EFFECT ON

INSTRUMENT PARAMETERS

TUBE TARGET	Cr
kV	50
mA	36
COUNTER	PF
COLLIMATOR	COARSE
HELIUM FLOW	5 c.f.h.
P10 FLOW	0.1 c.f.h.
CRYSTAL	PET
HIGH VOLTAGE DETECTOR	3.50 HELIPOT
GAIN	10
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	65.53
2θ Background	68.50
ω	0.16
COUNTING TIME	20 sec.

4.2.2.1 EFFECT OF M ON Cl

(a)

Solution	C_{Cl}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
Cl-1	0.02158	0.97842	6765	8588
Cl-2	0.03237	0.96763	10072	12786
Cl-3	0.04316	0.95684	13341	16936
Cl-4	0.05395	0.94605	16548	21008
Cl-5	0.06474	0.93526	19735	25054
Cl-6	0.08632	0.91368	25998	33004

(b)

		α_{ClM}
Solution	Cl-1/Solution Cl-6	-0.39009
"	Cl-1/ " Cl-5	-0.39977
"	Cl-1/ " Cl-4	-0.40811
"	Cl-2/ " Cl-6	-0.38488
"	Cl-2/ " Cl-5	-0.39475
"	Cl-3/ " Cl-6	-0.38432

average α_{ClM} = -0.39^3

std. dev. = $\pm 0.01^6$

(c)

Solution	C_{Cl}	C_M	$I^{My}_{ClK\alpha}$ (cps)	$I^{Corr.\ by\ M}_{ClK\alpha}$ (cps)	$I^{o}_{ClK\alpha}$ (cps)
Cl-1	0.02158	0.97842	8588	5279	244626
Cl-2	0.03237	0.96763	12786	7914	244481
Cl-3	0.04316	0.95684	16936	10554	244542
Cl-4	0.05395	0.94605	21008	13181	244319
Cl-5	0.06474	0.93526	25054	15826	244462
Cl-6	0.08632	0.91368	33004	21129	244774

average $I^{o}_{ClK\alpha}$ = 244500 cps

std. devn. = ± 500 cps

(d)

Solution	C_{Cl}	$I^{Corr.}_{ClK\alpha}$ (cps)	$C^{Back\ cal.}_{ClK\alpha}$	Abs. error	% error
Cl-1	0.02158	5279	0.02159	0.00001	0.05
Cl-2	0.03237	7914	0.03236	0.00001	0.03
Cl-3	0.04316	10554	0.04316	0.00000	0.00
Cl-4	0.05395	13181	0.05390	0.00005	0.09
Cl-5	0.06474	15826	0.06472	0.00002	0.03
Cl-6	0.08632	21129	0.08641	0.00009	0.10

FIGURE ...2.1.1 (ClK_α)

Sample: 1/ C_{Cl} = 0.06474 in aqueous
2/ H_2O + HNO_3 aqueous

Chart Scale: 30K c.p.s.

Scan Speed: 1"/min

$I^{meas} = I_1^{2\theta} - I_2^{2\theta}$

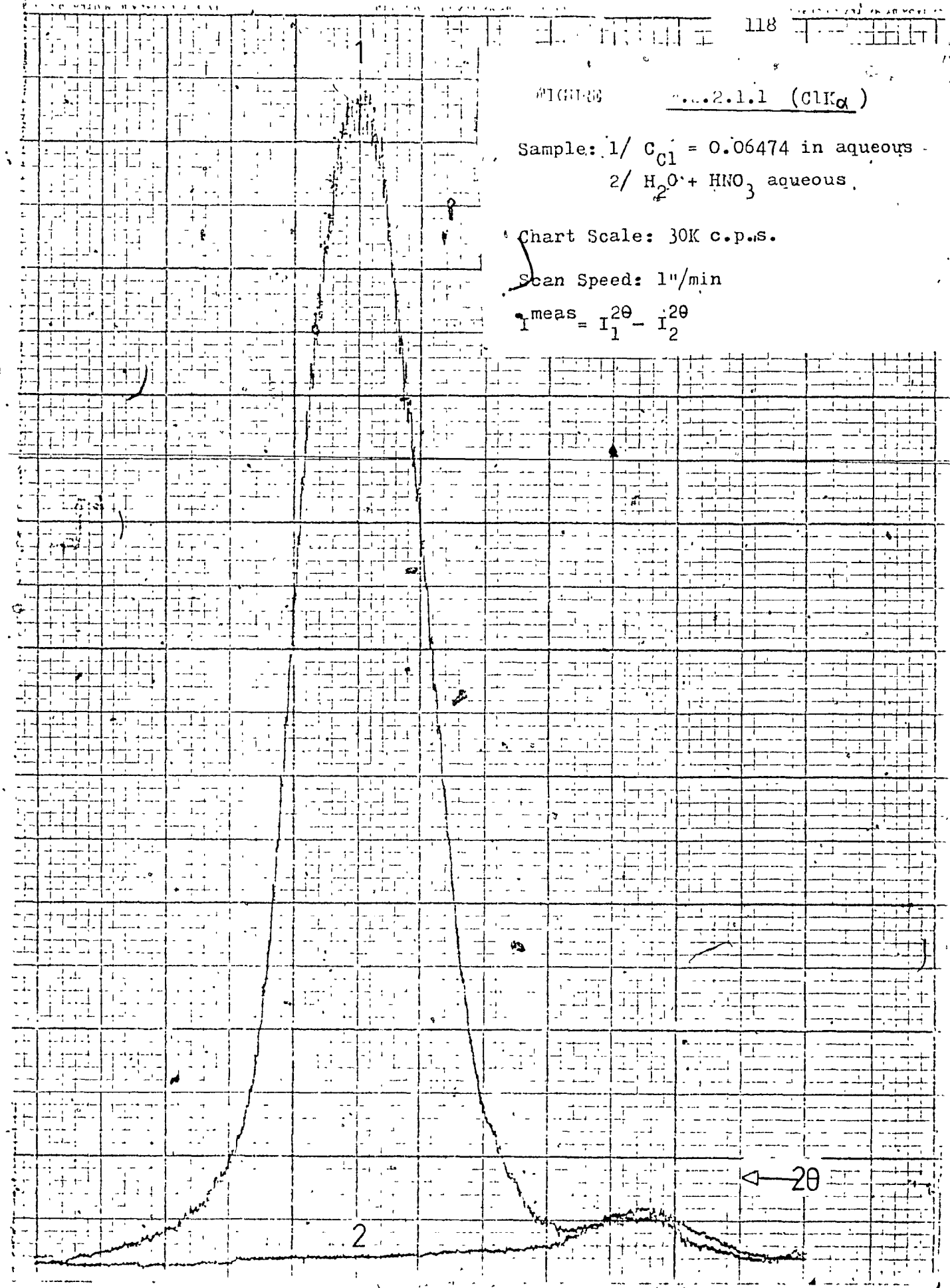
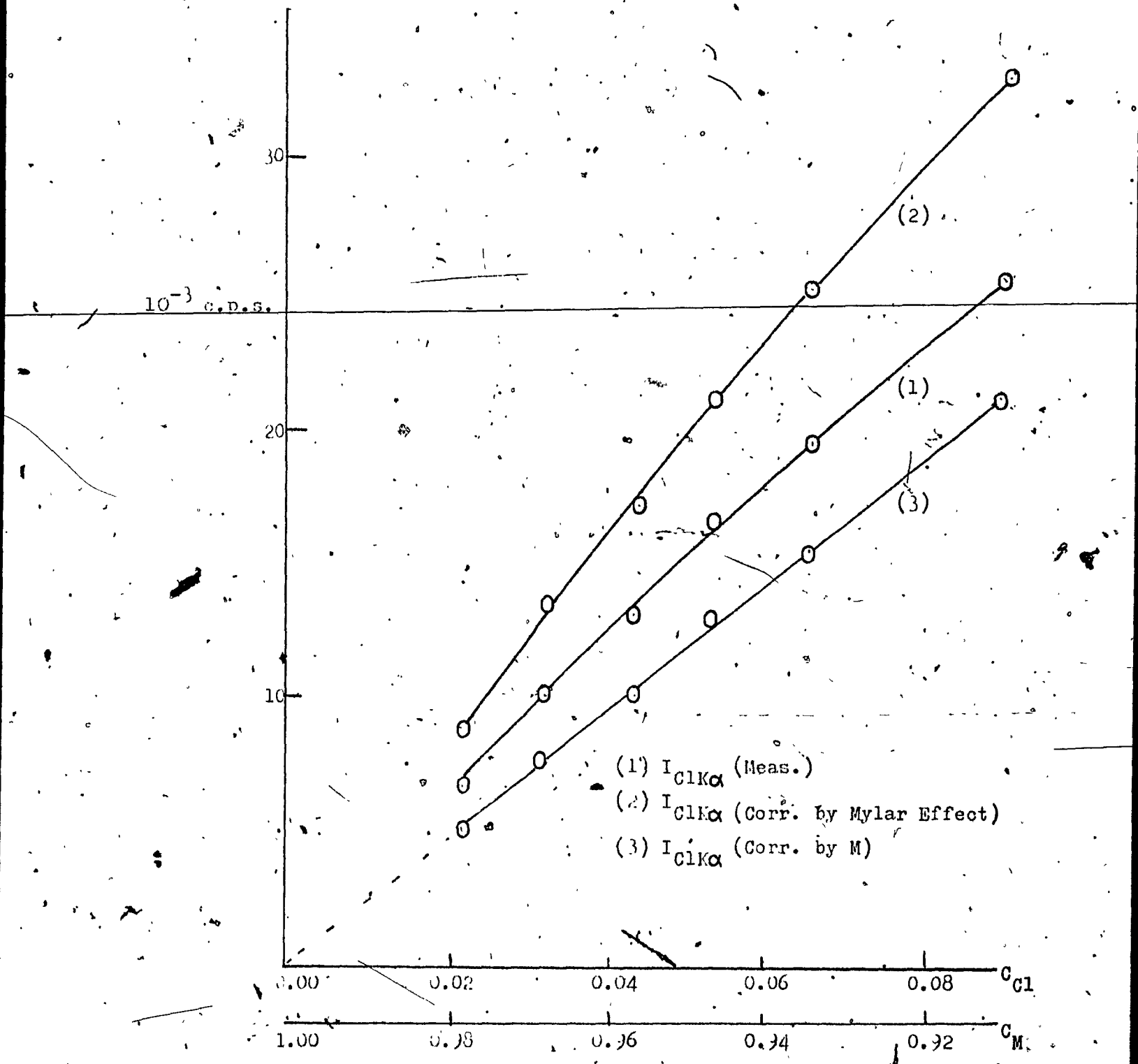


FIGURE 4.2.2.1.2

$I_{ClK\alpha}$ VERSUS C_{Cl} AND C_M



4.2.2.2 EFFECT OF Al AND M ON Cl

(a)

Solution	C_{Cl}	C_{Al}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
ClA-1	0.047510	0.00000	0.95249	16381	20736
ClA-2	0.047510	0.00500	0.94749	16351	20757
ClA-3	0.047510	0.01000	0.94249	16338	20741
ClA-4	0.047510	0.02000	0.93249	16300	20692
ClA-5	0.047510	0.02500	0.92749	16281	20668
ClA-6	0.047227	0.02982	0.92295	16172	20530

(b)

	α_{ClAl}
Solution ClA-1/Solution ClA-6	-0.24404
" ClA-1/ " ClA-5	-0.23805
" ClA-1/ " ClA-4	-0.23577
" ClA-2/ " ClA-6	-0.26149
" ClA-2/ " ClA-5	-0.25814
" ClA-3/ " ClA-6	-0.25264

average $\alpha_{ClAl} = -0.24^8$

std. devn. $= \pm 0.01^1$

(c)

Solution	C_{Cl}	C_{Al}	C_M	(cps) $I^{My}_{ClK\alpha}$	(cps) $I^{Corr.\ by\ M}_{ClK\alpha}$	(cps) $I^{Corr.}_{ClK\alpha}$	(cps) $I^{o}_{ClK\alpha}$
ClA-1	0.04751	0.00000	0.95249	20796	13011	13011	273868
ClA-2	0.04751	0.00500	0.94749	20757	13028	13002	273671
ClA-3	0.04751	0.01000	0.94249	20741	13059	13007	273776
ClA-4	0.04751	0.02000	0.93249	20692	13109	13006	273761
ClA-5	0.04751	0.02500	0.92749	20668	13134	13006	273759
ClA-6	0.04723	0.02982	0.92295	20530	13083	12932	273816

average $I^{o}_{ClK\alpha}$ = 273800 cps

std. devn. = ± 100 cps

(d)

Solution	C_{Cl}	$I^{Corr.}_{ClK\alpha}$ (cps)	$C^{Back\ cal.}_{Cl}$	Abs. error	% error
ClA-1	0.04751	13011	0.04752	0.00001	0.02
ClA-2	0.04751	13002	0.04749	0.00002	0.04
ClA-3	0.04751	13007	0.04751	0.00000	0.00
ClA-4	0.04751	13006	0.04750	0.00001	0.04
ClA-5	0.04751	13006	0.04750	0.00001	0.04
ClA-6	0.04723	12932	0.04723	0.00000	0.00

FIGURE 4.2.2.1 (ClKα)

Sample: 1/ C_{Cl} = 0.04316 in aqueous .

C_{Al} = 0.01

2/ C_{Al} = 0.01 in aqueous

Chart Scale: 30K c. p.s.

2θ Scan Speed: 1°/min

$I^{meas} = I_1^{2\theta} - I_2^{2\theta}$

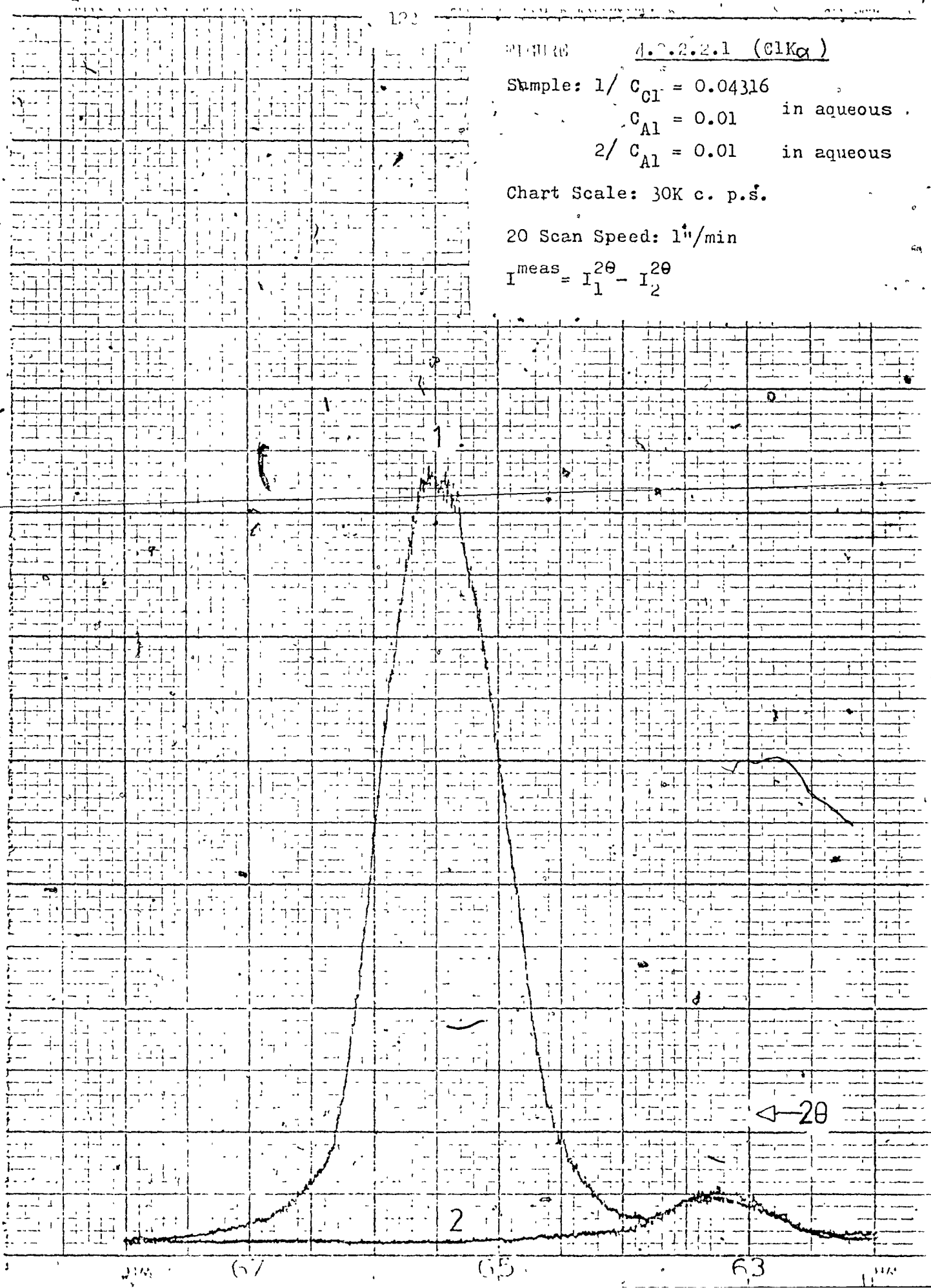
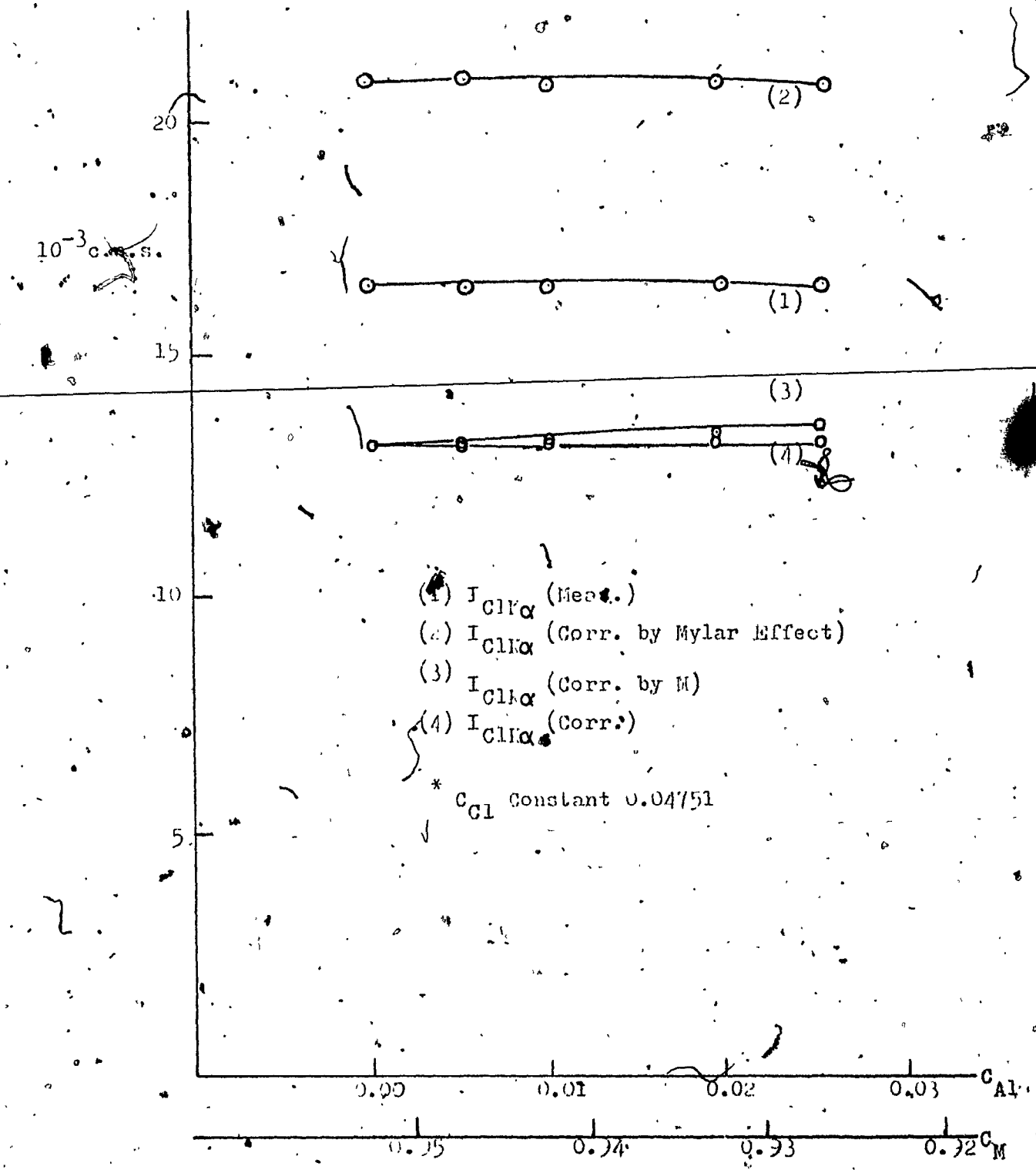


FIGURE 4...2. .2

$I_{ClK\alpha}$ VERSUS C_{Al} AND C_M



4.2.2.3 EFFECT OF Mn AND M ON Cl

(a)

Solution	C_{Cl}	C_{Mn}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
ClM-1	0.02772	0.00000	0.97228	8749	11107
ClM-2	0.02772	0.01000	0.96228	8635	10962
ClM-3	0.02772	0.02000	0.95228	8522	10819
ClM-4	0.02772	0.03000	0.94228	8412	10679
ClM-5	0.02772	0.04000	0.93228	8302	10539
ClM-6	0.02772	0.05000	0.92228	8209	10421

(b)

		α_{ClMn}
Solution	ClM-1/Solution ClM-6	0.41868
"	ClM-1/ " ClM-5	0.43769
"	ClM-1/ " ClM-4	0.43064
"	ClM-2/ " ClM-6	0.41766
"	ClM-2/ " ClM-5	0.44302
"	ClM-3/ " ClM-6	0.41236

average $\alpha_{ClMn} = 0.42^7$

std. devn. $= \pm 0.01^2$

(c)

Solution	C_{Cl}	C_{Mn}	C_M	$I^{My}_{ClK\alpha}$ (cps)	$I^{Corr.}_{ClK\alpha}$ (cps)	by M	$I^{Corr}_{ClK\alpha}$ (cps)	$I^{o}_{ClK\alpha}$ (cps)
ClM-1	0.02772	0.00000	0.97228	11107	6854	6854		247258
ClM-2	0.02772	0.01000	0.96228	10962	6808	6855		247294
ClM-3	0.02772	0.02000	0.95228	10819	6762	6854		247258
ClM-4	0.02772	0.03000	0.94228	10679	6716	6853		247222
ClM-5	0.02772	0.04000	0.93228	10539	6670	6850		247114
ClM-6	0.02772	0.05000	0.92228	10421	6630	6858		247403

average $I^{o}_{ClK\alpha}$ = 247260 cps

std. devn. = ± 90 cps

(d)

Solution	C_{Cl}	$I^{Corr}_{ClK\alpha}$ (cps)	$C^{Back\ cal.}_{Cl}$	Abs. error	% error
ClM-1	0.02772	6854	0.02772	0.00000	0.00
ClM-2	0.02772	6855	0.02772	0.00000	0.00
ClM-3	0.02772	6854	0.02772	0.00000	0.00
ClM-4	0.02772	6853	0.02771	0.00000	0.04
ClM-5	0.02772	6850	0.02770	0.00002	0.08
ClM-6	0.02772	6858	0.02774	0.00002	0.08

FIGURE 4.2.2.3.1 ($ClK\alpha$)

Sample: 1/ C_{Cl} = 0.02772
C_{Mn} = 0.01 in aqueous

2/ C_{Mn} = 0.01 in aqueous

Chart Scale: 30K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = I_1^{2\theta} - I_2^{2\theta}$

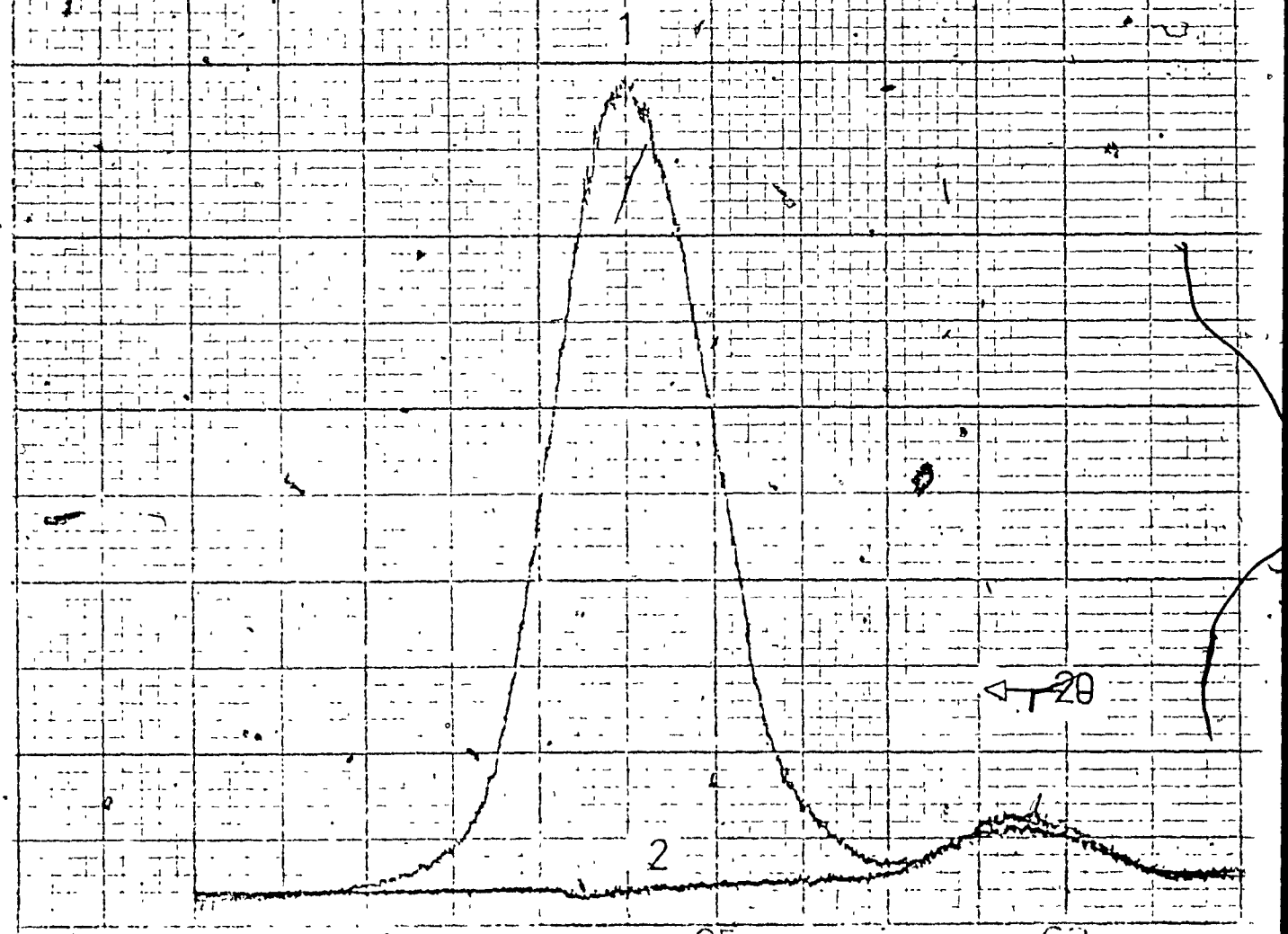
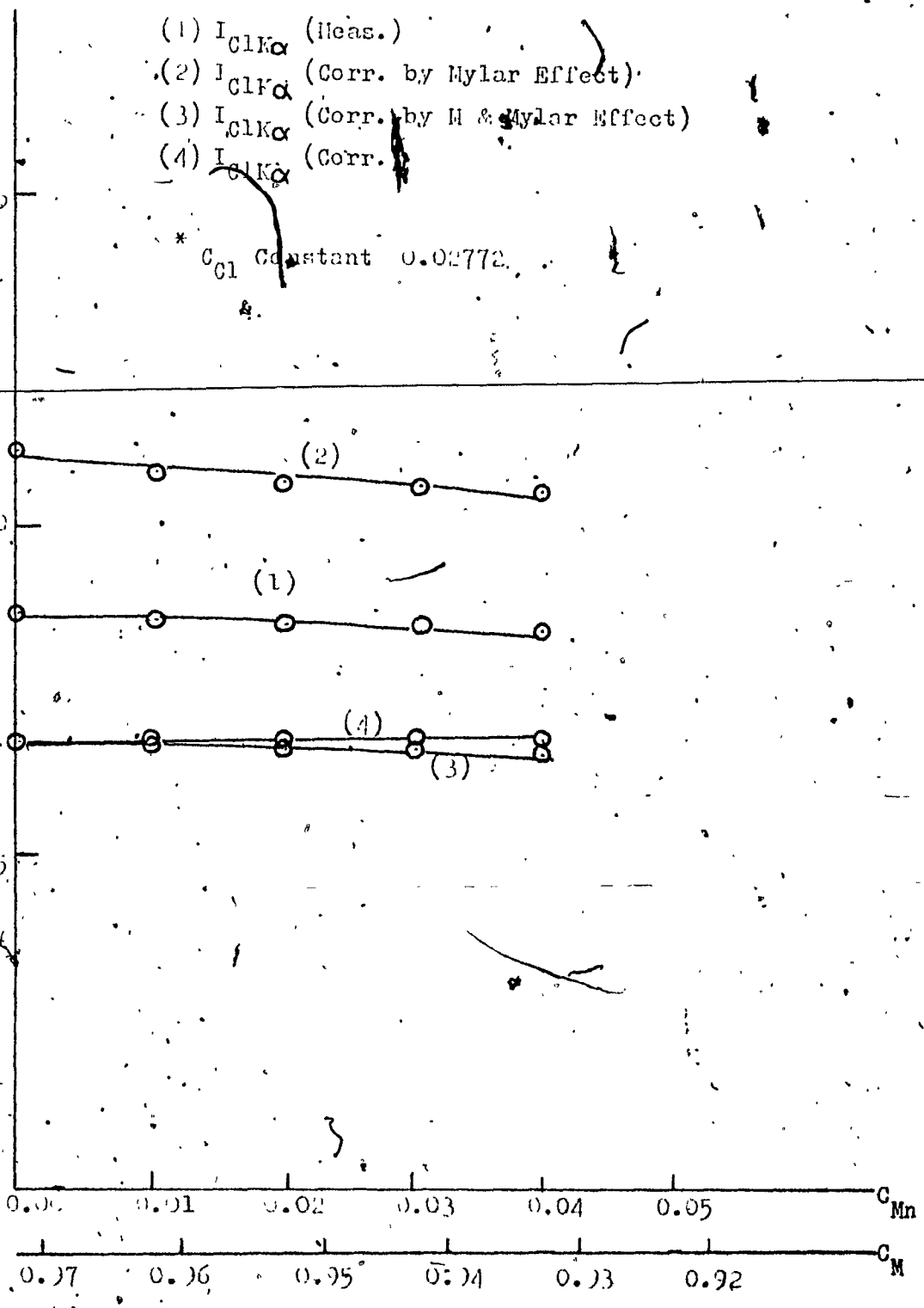


FIGURE 4.2...3.2

$I_{ClK\alpha}$ VERSUS C_{Mn} AND C_M

(1) $I_{ClK\alpha}$ (Meas.)
(2) $I_{ClK\alpha}$ (Corr. by Mylar Effect)
(3) $I_{ClK\alpha}$ (Corr. by M & Mylar Effect)
(4) $I_{ClK\alpha}$ (Corr.

* C_{Cl} Constant 0.02772



4.2.2.4 EFFECT OF Fe AND M ON Cl

(a)

Solution	C_{Cl}	C_{Fe}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
ClF-1	0.02772	0.00000	0.97228	8712	11060
ClF-2	0.02772	0.01000	0.96228	8567	10876
ClF-3	0.02772	0.02000	0.95228	8420	10689
ClF-4	0.02772	0.03000	0.94228	8297	10533
ClF-5	0.02772	0.04000	0.93228	8167	10368
ClF-6	0.02772	0.05000	0.92228	8058	10229

(b)

		α_{ClFe}
Solution	ClF-1/Solution ClF-6	0.60689
"	ClF-1/ " ClF-5	0.64183
"	ClF-1/ " ClF-4	0.63541
"	ClF-2/ " ClF-6	0.59772
"	ClF-2/ " ClF-5	0.63083
"	ClF-3/ " ClF-6	0.55985 ---(Reject)

average α_{ClFe} = 0.62^3

std. devn. = $\pm\ 0.01^9$

(c)

Solution	C_{Cl}	C_{Fe}	C_M	(cps) $I^{My}_{ClK\alpha}$	(cps) $I^{Corr.\ by\ M}_{ClK\alpha}$	(cps) $I^{Corr.}_{ClK\alpha}$	(cps) $I^{o}_{ClK\alpha}$
ClF-1	0.02772	0.00000	0.97228	11060	6825	6825	246212
ClF-2	0.02772	0.01000	0.96228	10876	6755	6823	246140
ClF-3	0.02772	0.02000	0.95228	10689	6681	6814	245815
ClF-4	0.02772	0.03000	0.94228	10533	6625	6822	246104
ClF-5	0.02772	0.04000	0.93228	10368	6562	6820	246032
ClF-6	0.02772	0.05000	0.92228	10229	6514	6833	246500

average $I^{o}_{ClK\alpha}$ = 246100 cps

std. devn. = ± 200 cps

(d)

Solution	C_{Cl}	$I^{Corr.}_{ClK\alpha}$ (cps)	Back cal. C_{Cl}	Abs. error	% error
ClF-1	0.02772	6825	0.02773	0.00001	0.04
ClF-2	0.02772	6823	0.02772	0.00000	0.00
ClF-3	0.02772	6814	0.02769	0.00003	0.11
ClF-4	0.02772	6822	0.02772	0.00000	0.00
ClF-5	0.02772	6820	0.02771	0.00001	0.04
ClF-6	0.02772	6833	0.02777	0.00005	0.18

FIGURE → 1.2.2.4.1 (ClK_α)

Sample: 1/ C_{Cl} = 0.02772
C_{Fe} = 0.01 in aqueous

2/ C_{Fe} = 0.01 in aqueous

Chart Scale: 30 K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = I_1^{2\theta} - I_2^{2\theta}$

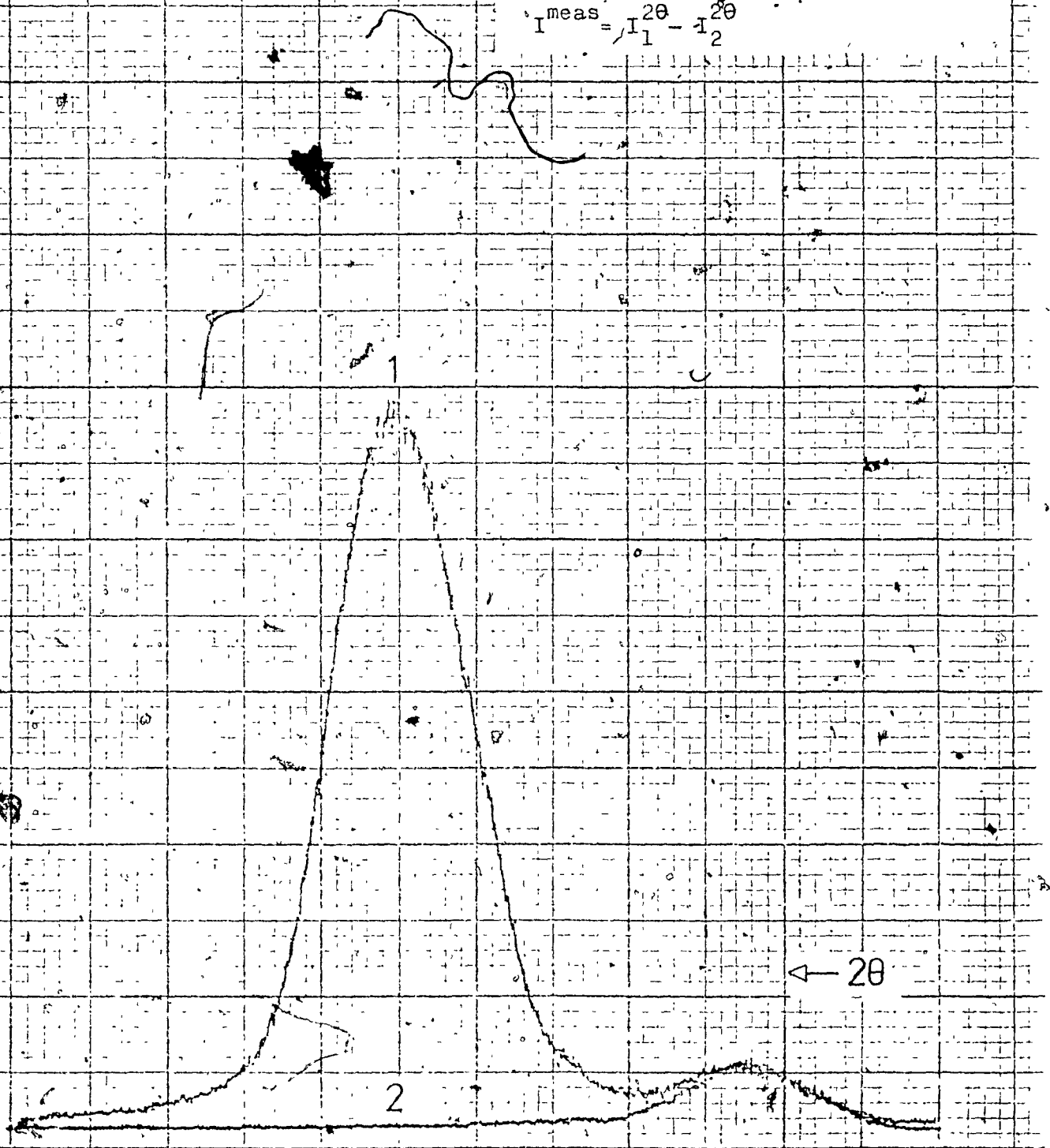
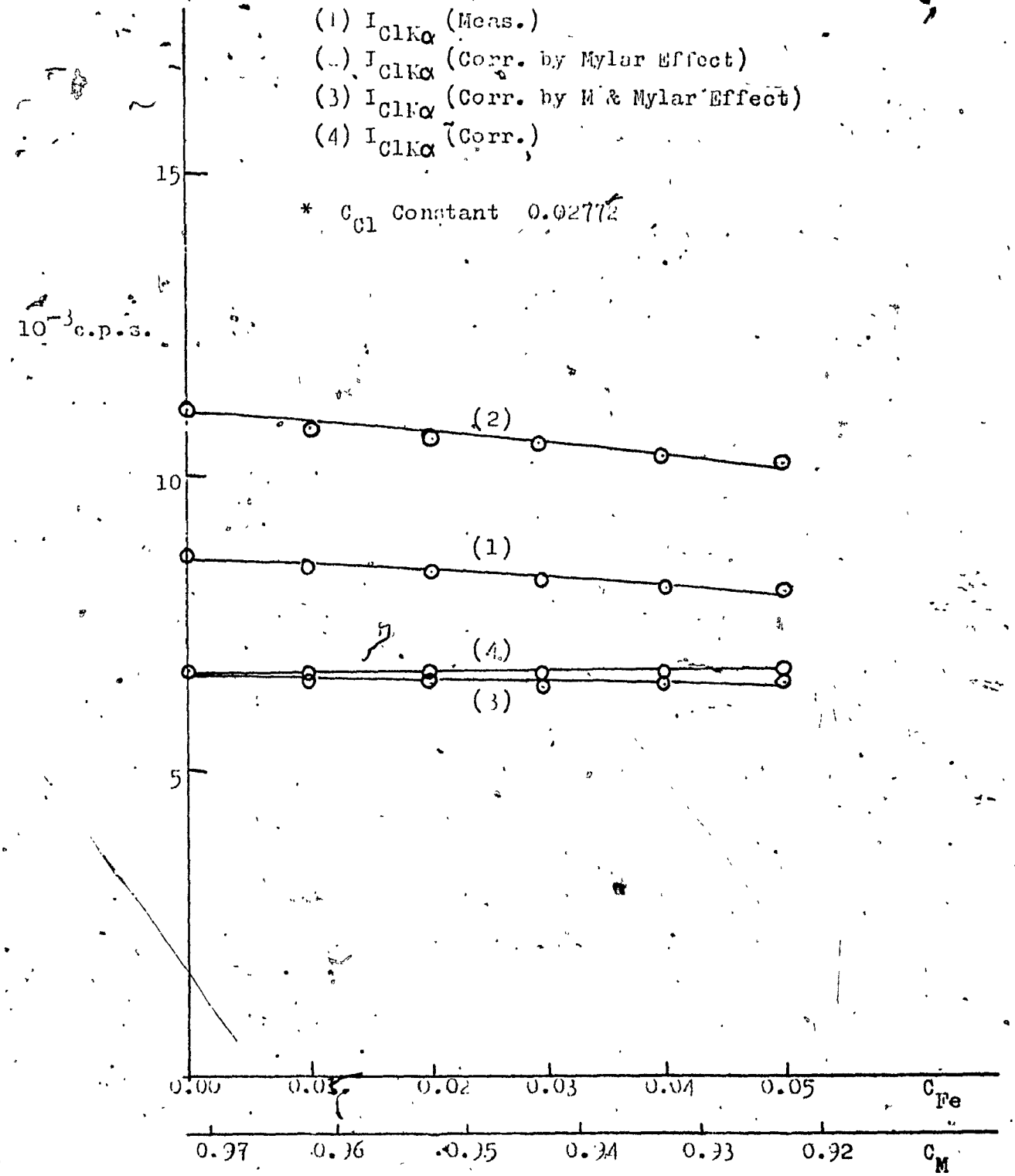


FIGURE 4.2.2.4.2

$I_{ClK\alpha}$ VERSUS C_{Fe} AND C_M



4.2.2.5 EFFECT OF Ni AND M ON Cl

(a)

Solution	C_{Cl}	C_{Ni}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
ClN-1	0.02772	0.00000	0.97228	8712	11060
ClN-2	0.02772	0.01000	0.96228	8543	10845
ClN-3	0.02772	0.02000	0.95228	8380	10638
ClN-4	0.02772	0.03000	0.94228	8225	10445
ClN-5	0.02772	0.04000	0.93228	8073	10249
ClN-6	0.02772	0.05000	0.92228	7918	10052

(b)

		α_{ClNi}
Solution	ClN-1/Solution ClN-6	0.84387
"	ClN-1/ " ClN-5	0.82701
"	ClN-1/ " ClN-4	0.82365
"	ClN-2/ " ClN-6	0.84779
"	ClN-2/ " ClN-5	0.82607
"	ClN-3/ " ClN-6	0.85389

average $\alpha_{ClNi} = 0.83^7$

std. devn. $= \pm 0.01^3$

(c)

Solution	C_{Cl}	C_{Ni}	C_M	(cps) $I^{My}_{ClK\alpha}$	(cps) $I^{Corr.\ by\ M}_{ClK\alpha}$	(cps) $I^{Corr.}_{ClK\alpha}$	(cps) $I^{o}_{ClK\alpha}$
ClN-1	0.02772	0.00000	0.97228	11060	6825	6825	246212
ClN-2	0.02772	0.01000	0.96228	10845	6735	6844	246897
ClN-3	0.02772	0.02000	0.95228	10638	6649	6827	246284
ClN-4	0.02772	0.03000	0.94228	10442	6567	6829	246356
ClN-5	0.02772	0.04000	0.93228	10249	6486	6829	246356
ClN-6	0.02772	0.05000	0.92228	10052	6401	6832	246104

average $I^{o}_{ClK\alpha}$ = 246400 cps

std. devn. = ± 300 cps

(d)

Solution	C_{Cl}	$I^{Corr.}_{ClK\alpha}$ (cps)	$C^{Back\ cal.}_{Cl}$	Abs. error	% error
ClN-1	0.02772	6825	0.02771	0.00001	0.04
ClN-2	0.02772	6844	0.02779	0.00007	0.25
ClN-3	0.02772	6827	0.02772	0.00000	0.00
ClN-4	0.02772	6829	0.02773	0.00001	0.04
ClN-5	0.02772	6829	0.02773	0.00001	0.04
ClN-6	0.02772	6822	0.02770	0.00002	0.08

FIGURE 4...2..5.1 ($ClK\alpha$)

Sample: 1/ C_{Cl} = 0.02772 in aqueous
C_{Ni} = 0.01

2/ C_{Ni} = 0.01 in aqueous

Chart Scale: 30 K cps

2θ Scan Speed: 1"/min

$I^{meas} = I_1^{2\theta} - I_2^{2\theta}$

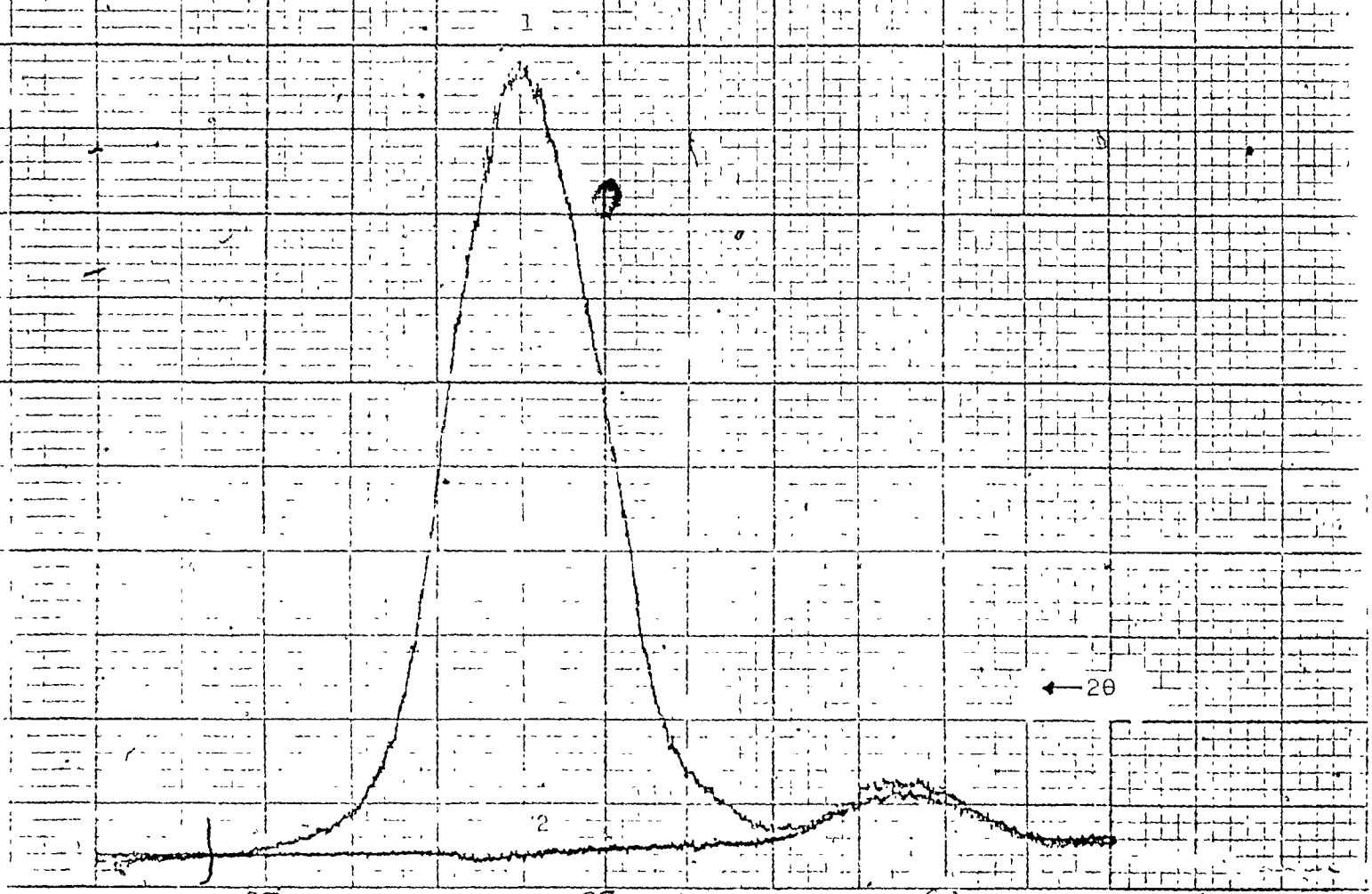
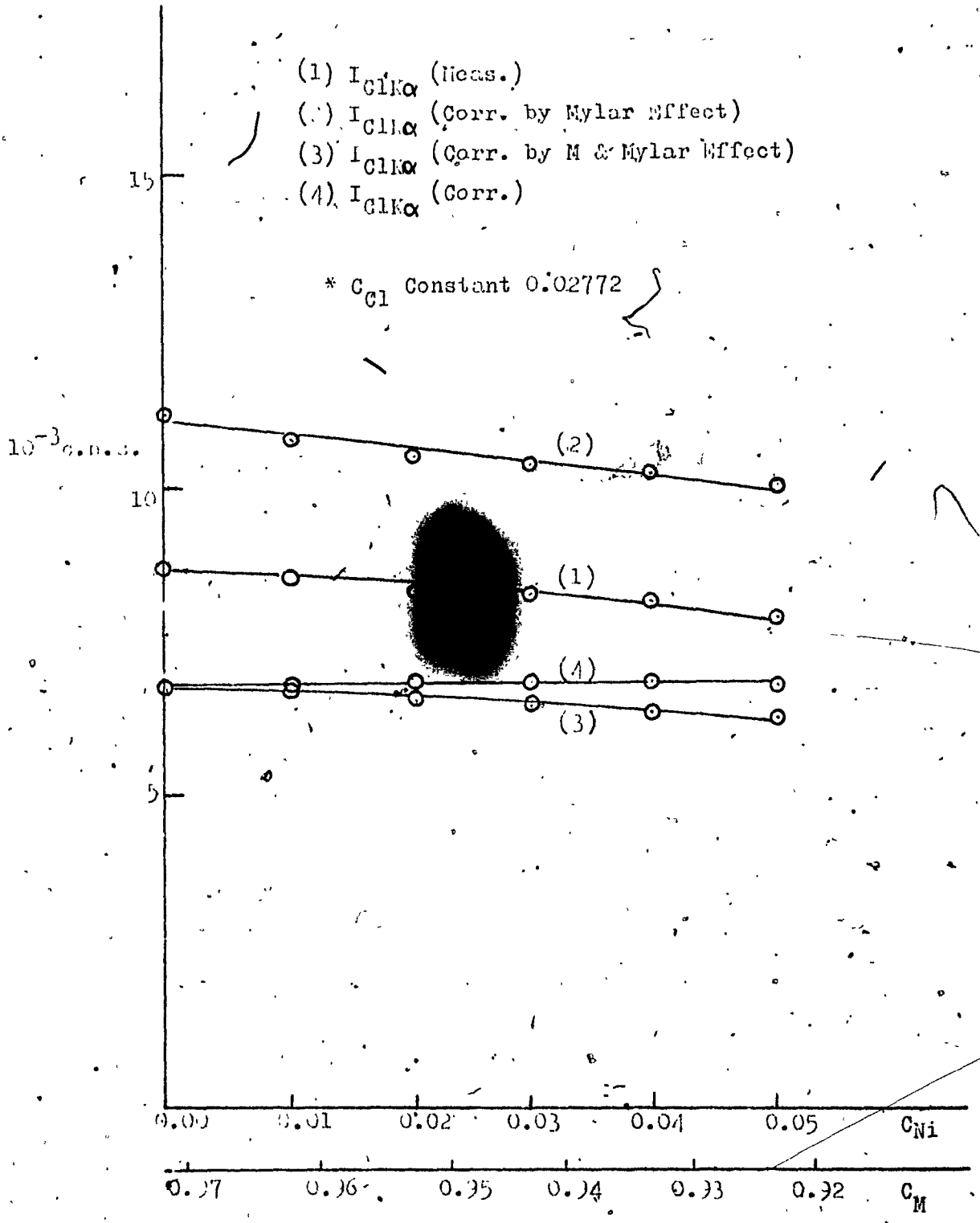


FIGURE 4.2.2.5.2

$I_{ClK\alpha}$ VERSUS C_{Ni} AND C_M



4.2.2.6 EFFECT OF Cu AND M ON Cl

(a)

Solution	C_{Cl}	C_{Cu}	C_M	$I^{meas}_{ClK\alpha}$ (cps)	$I^{My}_{ClK\alpha}$ (cps)
ClC-1	0.02772	0.00000	0.97228	8590	10905
ClC-2	0.02772	0.01000	0.96228	8413	10680
ClC-3	0.02772	0.02000	0.95228	8244	10466
ClC-4	0.02772	0.03000	0.94228	8077	10254
ClC-5	0.02772	0.04000	0.93228	7926	10062
ClC-6	0.02772	0.05000	0.92228	7771	9865

(b)

				α_{ClCu}
Solution	ClC-1/	Solution	ClC-6	0.90737
"	ClC-1/	"	ClC-5	0.89876
"	ClC-1/	"	ClC-4	0.91217
"	ClC-2/	"	ClC-6	0.90766
"	ClC-2/	"	ClC-5	0.89604
"	ClC-3/	"	ClC-6	0.91246

average $\alpha_{ClCu} = 0.90^6$

std. devn. $= \pm 0.01^0$

(c)

Solution	C_{Cl}	C_{Cu}	C_M	$I^{My}_{ClK\alpha}$ (cps)	$I^{Corr.\ by\ M}_{ClK\alpha}$ (cps)	$I^{Corr.}_{ClK\alpha}$ (cps)	$I^{o}_{ClK\alpha}$ (cps)
ClC-1	0.02772	0.00000	0.97228	10905	6730	6730	242785
ClC-2	0.02772	0.01000	0.96228	10680	6633	6730	242785
ClC-3	0.02772	0.02000	0.95228	10466	6541	6731	242821
ClC-4	0.02772	0.03000	0.94228	10254	6449	6728	242712
ClC-5	0.02772	0.04000	0.93228	10062	6368	6733	242893
ClC-6	0.02772	0.05000	0.92228	9865	6282	6729	242749

average $I^{o}_{ClK\alpha}$ = 242790 cps

std. devn. = ± 60 cps

(d)

Solution	C_{Cl}	$I^{Corr.}_{ClK\alpha}$ (cps)	$C^{Back\ cal.}_{Cl}$	Abs. error	% error
ClC-1	0.02772	6730	0.02772	0.00000	0.00
ClC-2	0.02772	6730	0.02772	0.00000	0.00
ClC-3	0.02772	6731	0.02772	0.00000	0.00
ClC-4	0.02772	6728	0.02771	0.00001	0.04
ClC-5	0.02772	6733	0.02773	0.00001	0.04
ClC-6	0.02772	6729	0.02772	0.00000	0.00

FIGURE 4.2.2.6.1 (ClK_α)

Sample: 1/ C_{Cl}=0.02772
C_{Cu}=0.01 in aqueous

2/ C_{Cu}=0.015 in aqueous

3/ H_2O+HNO_3 aqueous

Chart Scale: 30 K c.p.s.

2θ Scan Speed: 1"/min

$I^{meas} = I_1^{2\theta} - I_3^{2\theta}$

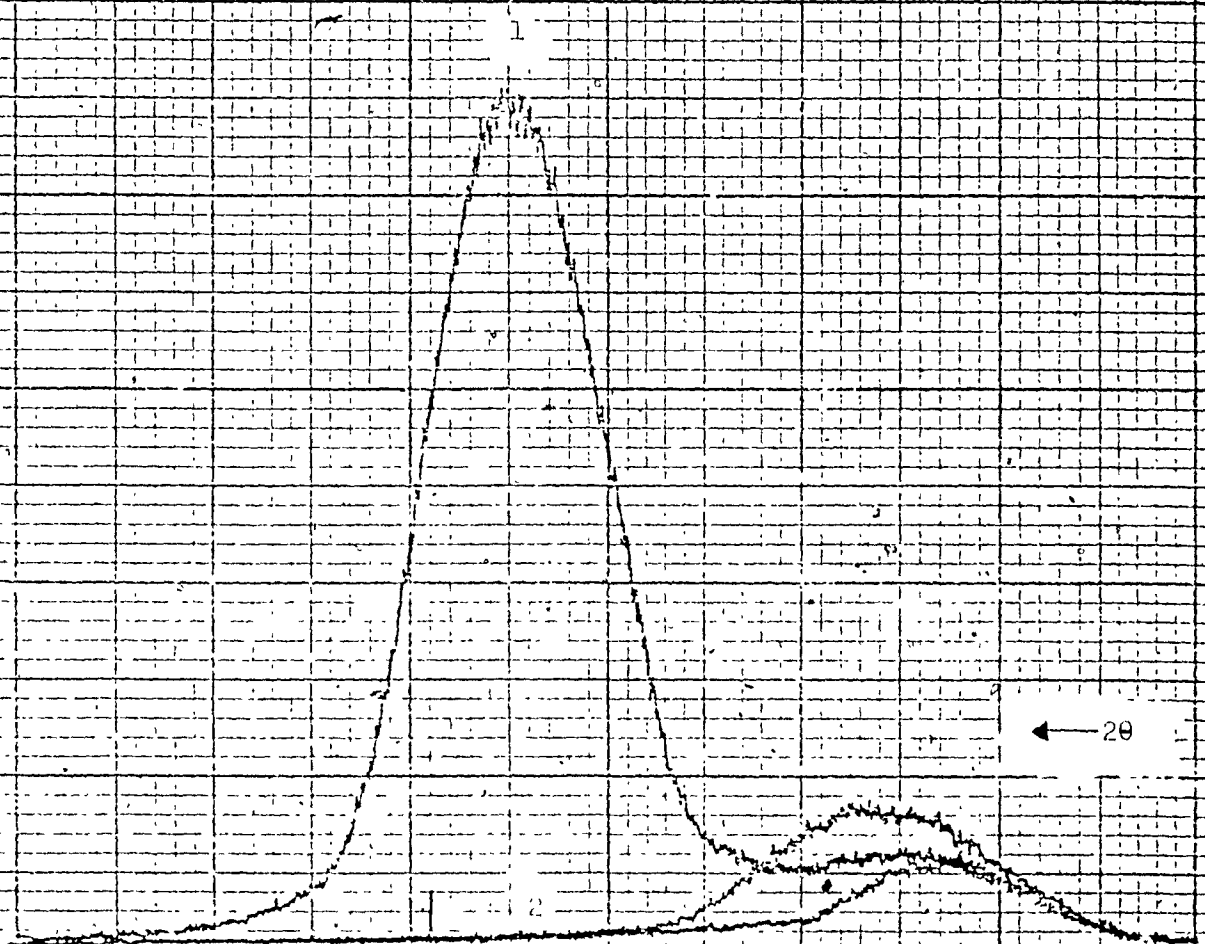
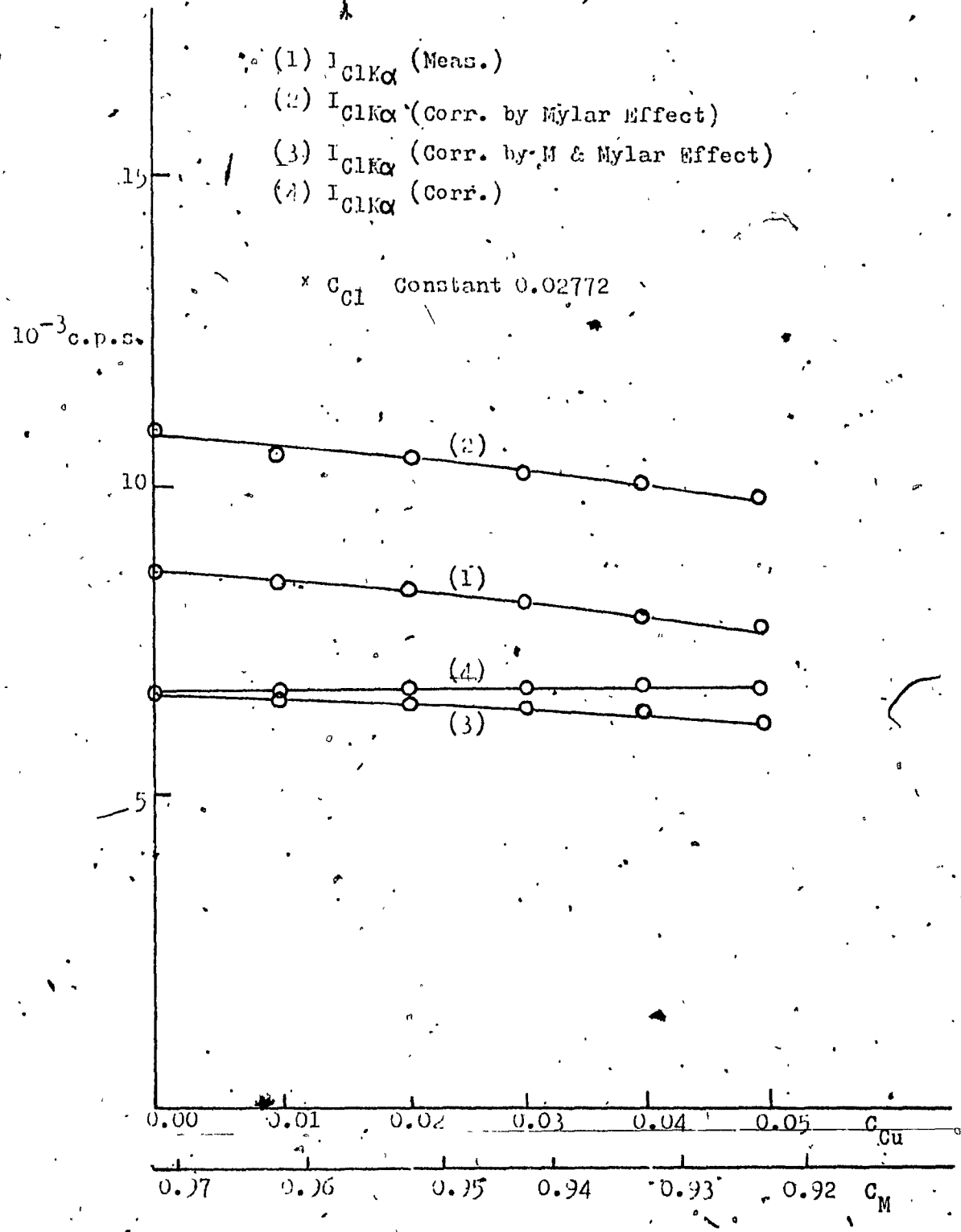


FIGURE 4.2.2.6.2

$I_{ClK\alpha}$ VERSUS C_{Cu} AND C_M



4.2.3 EFFECT OF Mn

INSTRUMENT PARAMETERS

TUBE TARGET	W
kV	50
mA	20
COUNTER	Scin.
COLLIMATOR	Fine
CRYSTAL	LiF
HIGH VOLTAGE DETECTOR	3.50 NELIPOT
GAIN	10
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	62.71
2θ Background	64.50
ω	0.08
COUNTING TIME	10 sec.

4.2.3.1 EFFECT OF M ON Mn

(a)

Solution	C_{Mn}	C_M	$I^{meas}_{MnK\alpha}$ (cps)	$I^{My}_{MnK\alpha}$ (cps)
M-1	0.01000	0.99000	8786	8981
M-2	0.02000	0.98000	17024	17404
M-3	0.04000	0.96000	30180	30853
M-4	0.06000	0.94000	41456	42381
M-5	0.08000	0.92000	51586	52736
M-6	0.10000	0.90000	59124	60442

(b)

		α_{MnM}
Solution	M-1/Solution M-6	-0.85090
"	M-1/ " M-5	-0.84520
"	M-1/ " M-4	-0.85165
"	M-2/ " M-6	-0.86064
"	M-2/ " M-5	-0.85657
"	M-3/ " M-6	-0.84942

average α_{MnM} = - 0.852[4]

std. devn. = ± 0.005[5]

(c)

Solution	C_{Mn}	C_M	(cps) $I^{My}_{MnK\alpha}$	(cps) $I^{Corr\ by\ M}_{MnK\alpha}$	(cps) $I^{o}_{MnK\alpha}$
M-1	0.01000	0.99000	8981	1402	140200
M-2	0.02000	0.98000	17404	2866	143300
M-3	0.04000	0.96000	30853	5606	140150
M-4	0.06000	0.94000	42381	8423	140383
M-5	0.08000	0.92000	52736	11380	142250
M-6	0.10000	0.90000	60442	14073	140730

average $I^{o}_{MnK\alpha}$ = 141200 cps

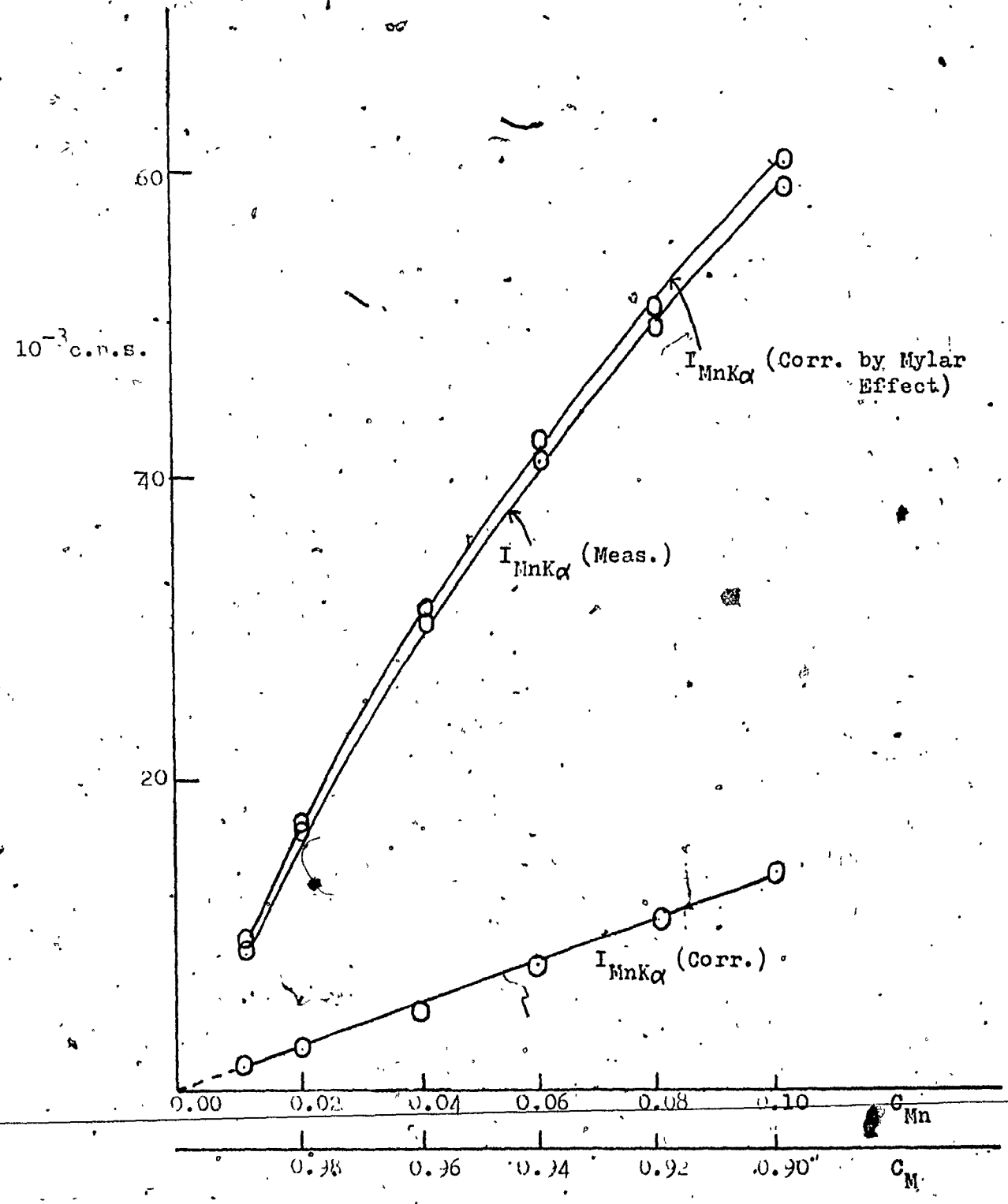
std. devn = ± 1300 cps

(d)

Solution	C_{Mn}	C_M	$I^{Corr}_{MnK\alpha}$ (cps)	$C^{Back\ cal.}_{Mn}$	Abs. error	% error
M-1	0.01000	0.99000	1402	0.00993	0.00007	0.70
M-2	0.02000	0.98000	2866	0.02030	0.00030	1.50
M-3	0.04000	0.96000	5606	0.03970	0.00030	0.75
M-4	0.06000	0.94000	8423	0.05965	0.00035	0.58
M-5	0.08000	0.92000	11380	0.08059	0.00059	0.74
M-6	0.10000	0.90000	14073	0.09967	0.00033	0.33

FIGURE 4...3.1

$I_{MnK\alpha}$ VERSUS C_{Mn} AND C_M



4.2.3.2 EFFECT OF Al AND M ON Mn

(a)

Solution	C_{Mn}	C_{Al}	C_M	$I^{meas}_{MnK\alpha}$ (cps)	$I^{My}_{MnK\alpha}$ (cps)
MA-1	0.02000	0.00000	0.98000	15585	15931
MA-2	0.02000	0.01000	0.97000	15395	15737
MA-3	0.02000	0.01500	0.96500	15280	15619
MA-4	0.02000	0.02000	0.96000	15194	15531
MA-5	0.02000	0.02500	0.95500	15092	15427
MA-6	0.01890	0.02836	0.95274	14329	14647

(b)

		α_{MnAl}
Solution	MA-1/Solution MA-6	-0.65653
"	MA-1/ " MA-5	-0.63724
"	MA-1/ " MA-4	-0.64038
"	MA-2/ " MA-6	-0.66049
"	MA-2/ " MA-5	-0.62884
"	MA-3/ " MA-6	-0.68330

average α_{MnAl} = - 0.65[1]

std. devn. = ± 0.02[0]

(c)

Solution	C_{Mn}	C_{Al}	C_M	(cps) $I^{My}_{MnK\alpha}$	(cps) $I^{Corr.\ by\ M}_{MnK\alpha}$	(cps) $I^{Corr.}_{MnK\alpha}$	(cps) $I^{o}_{MnK\alpha}$
MA-1	0.02000	0.00000	0.98000	15931	2623	2623	131150
MA-2	0.02000	0.01000	0.97000	15737	2725	2623	131150
MA-3	0.02000	0.01500	0.96500	15619	2771	2618	130900
MA-4	0.02000	0.02000	0.96000	15531	2822	2620	131000
MA-5	0.02000	0.02500	0.95500	15427	2869	2618	130900
MA-6	0.01890	0.02836	0.95274	14647	2752	2482	131294

average $I^{o}_{MnK\alpha}$ = 131100 cps

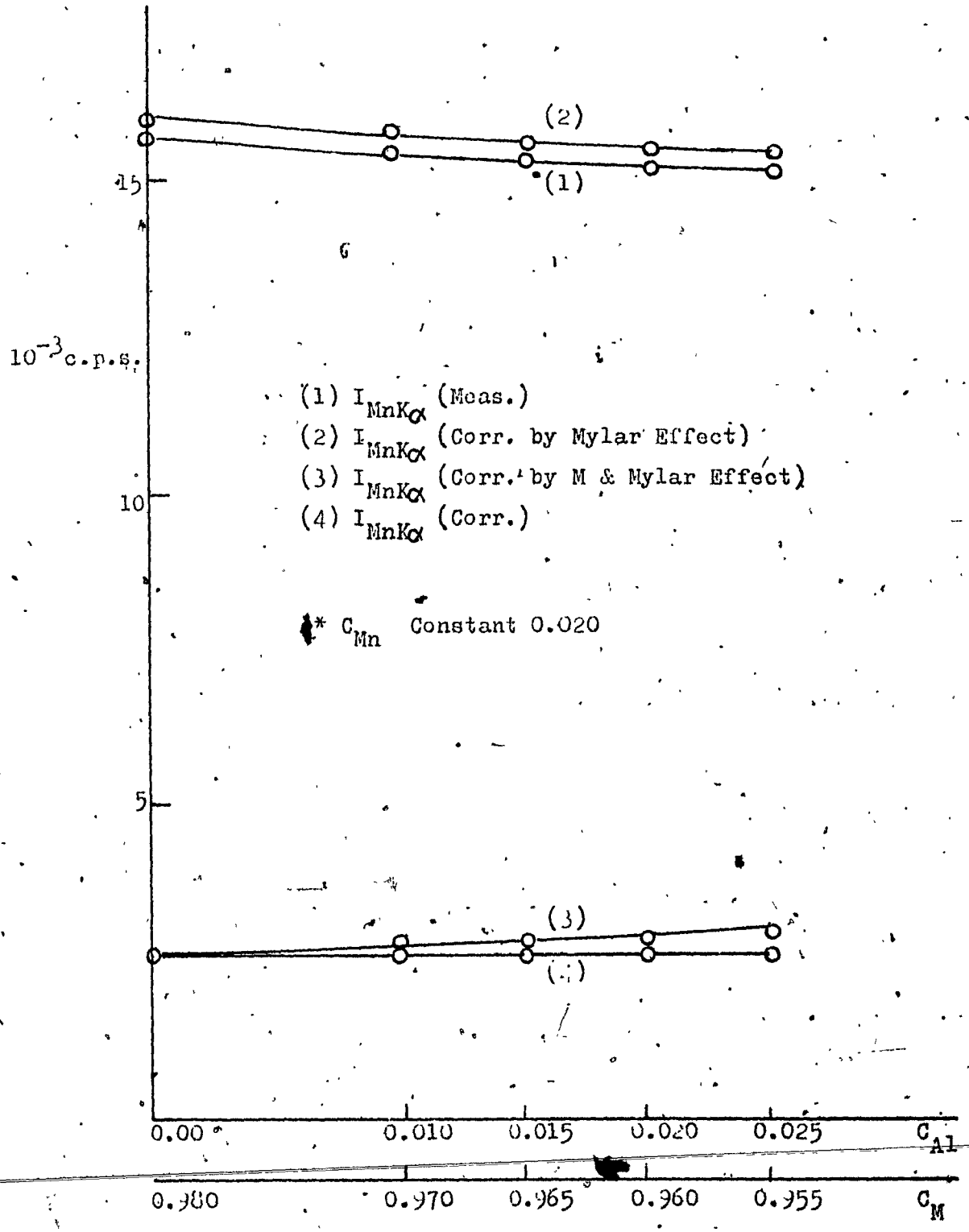
std. devn. = ± 200 cps

(d)

Solution	C_{Mn}	(cps) $I^{Corr.}_{MnK\alpha}$	$C^{Back\ cal.}_{Mn}$	Abs error	% error
MA-1	0.02000	2623	0.02001	0.00001	0.05
MA-2	0.02000	2623	0.02001	0.00001	0.05
MA-3	0.02000	2618	0.01997	0.00003	0.15
MA-4	0.02000	2620	0.01998	0.00002	0.10
MA-5	0.02000	2618	0.01997	0.00003	0.15
MA-6	0.01890	2482	0.01893	0.00003	0.16

FIGURE 4.2.3.2

$I_{MnK\alpha}$ VERSUS C_{Al} AND C_M



4.2.3.3 EFFECT OF Cl AND M ON Mn

(a)

Solution	C_{Mn}	C_{Cl}	C_M	$I^{meas}_{MnK\alpha}$ (cps)	$I^{My}_{MnK\alpha}$ (cps)
MCl-1	0.01000	0.00000	0.99000	8208	8391
MCl-2	0.01000	0.02158	0.96842	7037	7194
MCl-3	0.01000	0.04316	0.94684	6184	6322
MCl-4	0.01000	0.06474	0.92526	5478	5600
MCl-5	0.01000	0.08632	0.90368	4900	5009
MCl-6	0.01000	0.10791	0.88209	4442	4541

(b)

			α_{MnCl}
Solution	MCl-1/	Solution MCl-6	0.37430
"	MCl-1/	" MCl-5	0.36873
"	MCl-1/	" MCl-4	0.34944
"	MCl-2/	" MCl-6	0.38496
"	MCl-2/	" MCl-5	0.37848
"	MCl-3/	" MCl-6	0.42822--(Reject)

average $\alpha_{MnCl} = 0.37^1$

std. devn. $= \pm 0.01^4$

(c)

Solution	C_{Mn}	C_{Cl}	C_M	$I^{My}_{MnK\alpha}$ (cps)	$I^{Corr.\ by\ M}_{MnK\alpha}$ (cps)	$I^{Corr.}_{MnK\alpha}$ (cps)	$I^{o}_{MnK\alpha}$ (cps)
MCl-1	0.01000	0.00000	0.99000	8391	1310	1310	131000
MCl-2	0.01000	0.02158	0.96842	7194	1255	1313	131300
MCl-3	0.01000	0.04316	0.94684	6322	1220	1321	132100
MCl-4	0.01000	0.06474	0.92526	5600	1183	1318	131800
MCl-5	0.01000	0.08632	0.90368	5009	1151	1311	131100
MCl-6	0.01000	0.10791	0.88209	4541	1127	1308	130800

average $I^{o}_{MnK\alpha}$ = 131400 cps

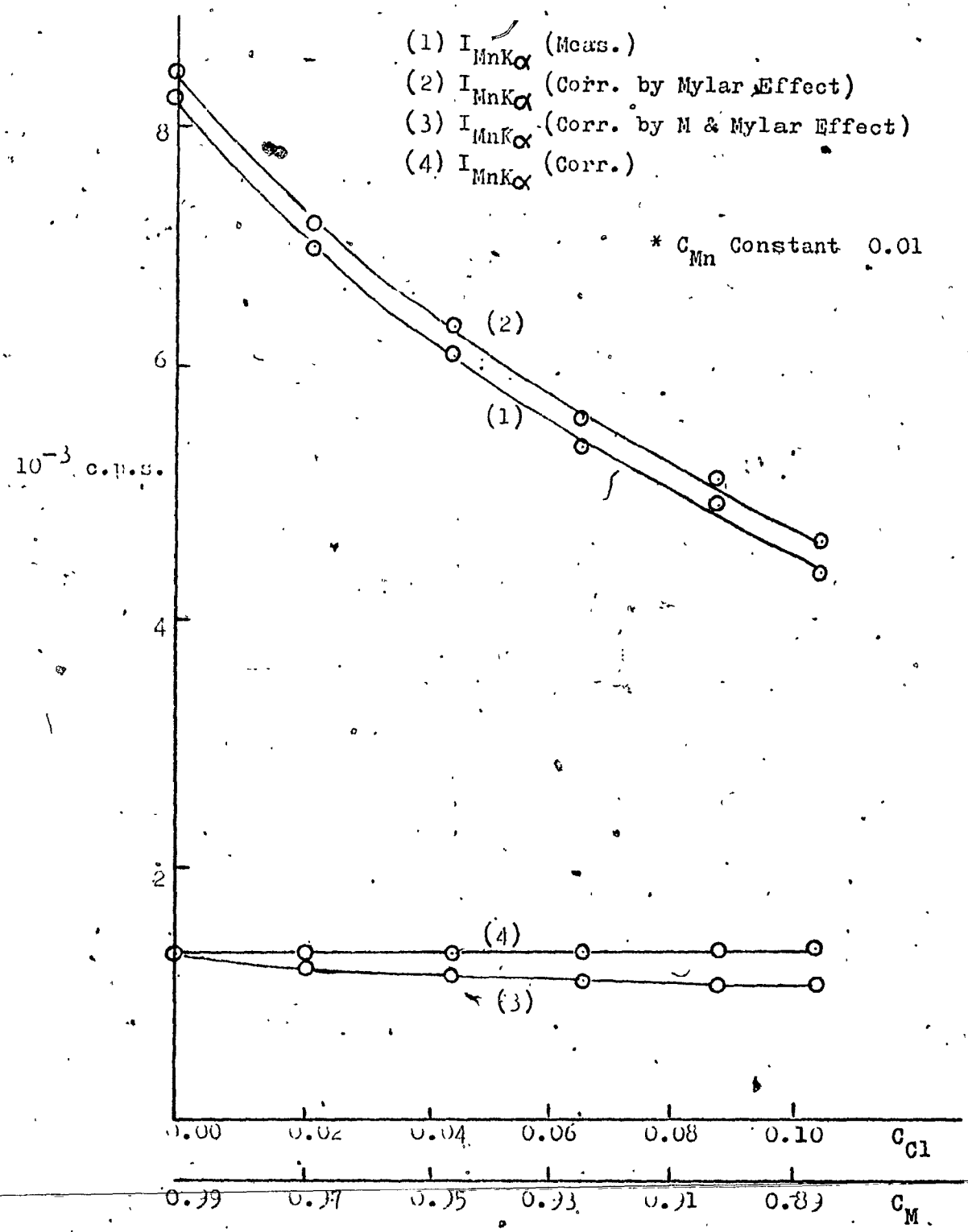
std. devn. = ± 500 cps

(d)

Solution	C_{Mn}	$I^{Corr.}_{MnK\alpha}$ (cps)	$C^{Back\ cal.}$	Abs. error	% error
MCl-1	0.01000	1310	0.00997	0.00003	0.30
MCl-2	0.01000	1313	0.01000	0.00000	0.00
MCl-3	0.01000	1321	0.01006	0.00006	0.60
MCl-4	0.01000	1318	0.01003	0.00003	0.30
MCl-5	0.01000	1311	0.00998	0.00002	0.20
MCl-6	0.01000	1308	0.00996	0.00004	0.40

FIGURE 3.3.3

$I_{MnK\alpha}$ VERSUS C_{Cl} AND C_M



4.2.4 EFFECT ON Fe

INSTRUMENT PARAMETER

TUBE TARGET	W
kV	50
mA	20
COUNTER	Scin.
COLLIMATOR	Fine
CRYSTAL	LiF
HIGH VOLTAGE DETECTOR	3.50
GAIN	10
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	57.45
2θ Background	56.40
ω	0.08
COUNTING TIME	10 sec.

4.2.4.1 EFFECT OF M ON Fe

(a)

Solution	C_{Fe}	C_M	$I^{meas}_{FeK\alpha}$ (cps)	$I^{My}_{FeK\alpha}$ (cps)
F-1	0.00500	0.99500	8775	8936
F-2	0.01000	0.99000	16512	16819
F-3	0.01500	0.98500	23546	23984
F-4	0.02000	0.98000	30031	30590
F-5	0.03000	0.97000	42509	43300
F-6	0.04000	0.96000	53044	54030
F-7	0.05000	0.95000	62320	63378

(b)

		α_{FeM}	
Solution	F-1/Solution F-7	-0.90516	
"	F-1/ " F-6	-0.90635	
"	F-1/ " F-5	-0.90914	
"	F-1/ " F-4	-0.92248	----(Reject)
"	F-2/ " F-7	-0.89898	
"	F-2/ " F-6	-0.89889	
"	F-2/ " F-5	-0.90009	
"	F-3/ " F-7	-0.89375	
"	F-3/ " F-6	-0.89200	
"	F-4/ " F-7	-0.88875	----(Reject)

average α_{FeM} = -0.900^5

std. devn. = $\pm 0.004^4$

(c)

Solution	C_{Fe}	C_M	$I^{My}_{FeK\alpha}$ (cps)	$I^{Corr.\ by\ M}_{FeK\alpha}$ (cps)	$I^{o}_{FeK\alpha}$ (cps)
F-1	0.005 00	0.99500	8936	930	186000
F-2	0.010 00	0.99000	16919	1825	182500
F-3	0.01500	0.98500	23984	2710	180666
F-4	0.02000	0.98000	30590	3595	179750
F-5	0.03000	0.97000	43300	5478	182600
F-6	0.04000	0.96000	54030	7322	183050
F-7	0.05000	0.95000	63378	9160	183200

average $I^{o}_{FeK\alpha}$ = 182500 cps

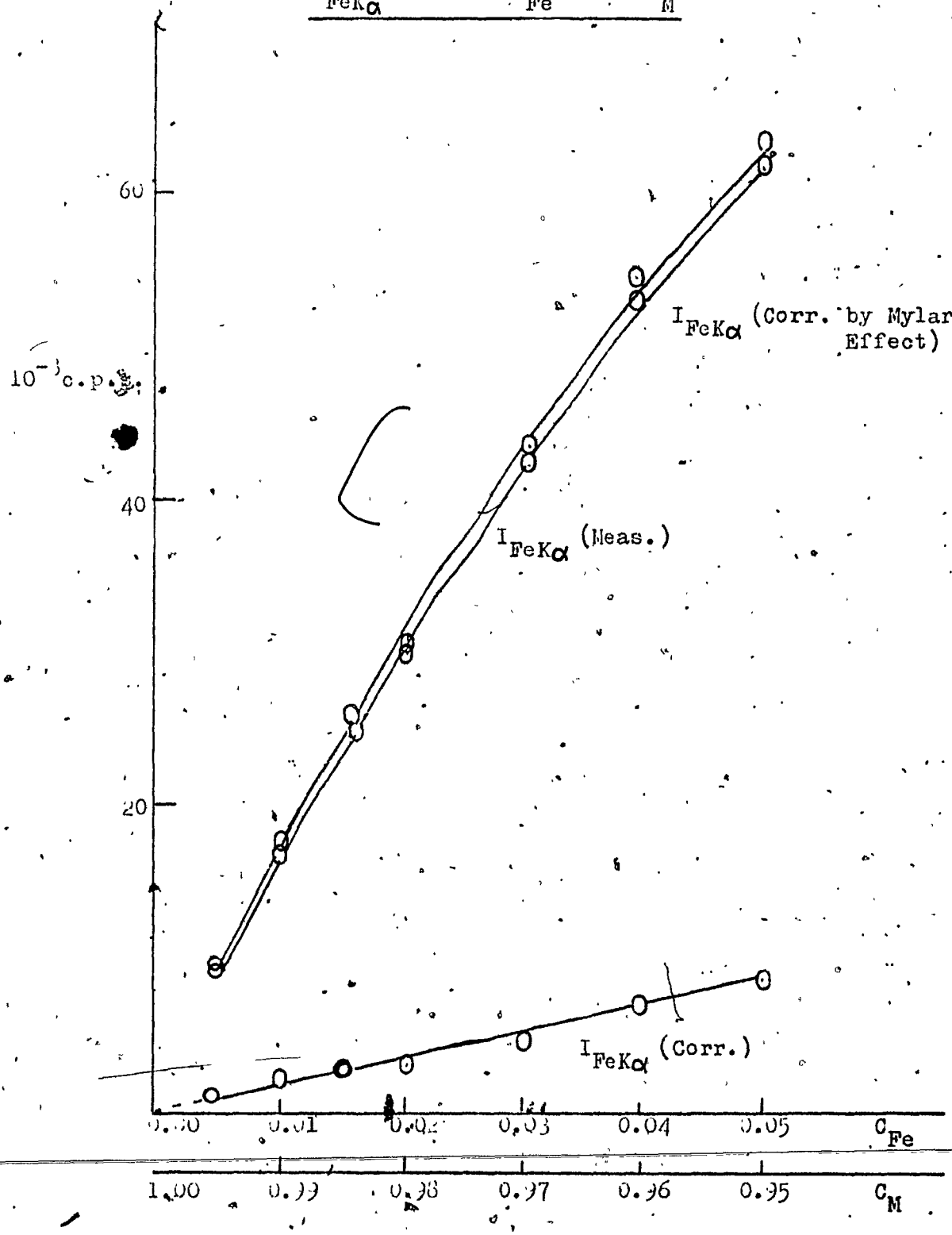
std. devn. = $\pm$ 1300 cps.

(d)

Solution	C_{Fe}	$I^{Corr.}_{FeK\alpha}$ (cps)	$C^{Back\ cal.}_{Fe}$	Abs. error	% error
F-1	0.00500	930	0.00510	0.00010	2.0
F-2	0.01000	1825	0.01000	0.00000	0.00
F-3	0.01500	2710	0.01485	0.00015	1.0
F-4	0.02000	3595	0.01970	0.00030	1.5
F-5	0.03000	5478	0.03002	0.00002	0.07
F-6	0.04000	7322	0.04012	0.00012	0.30
F-7	0.05000	9160	0.05019	0.00019	0.38

FIGURE 4.2.4.1

$I_{FeK\alpha}$ VERSUS C_{Fe} AND C_M



4.2.4.2 EFFECT OF Al AND M ON Fe

(a)

Solution	C_{Fe}	C_{Al}	C_M	$I^{meas}_{FeK\alpha}$ (cps)	$I^{My}_{FeK\alpha}$ (cps)
FA-1	0.02000	0.00000	0.98000	30745	31308
FA-2	0.02000	0.01000	0.97000	30221	30774
FA-3	0.02000	0.01500	0.96500	29984	30451
FA-4	0.02000	0.02000	0.96000	29747	30291
FA-5	0.02000	0.02500	0.95500	29487	30027
FA-6	0.01828	0.02742	0.95430	27324	27824

(b)

		α_{FeAl}
Solution	FA-1/Solution FA-6	-0.72210
"	FA-1/ " FA-5	-0.69997
"	FA-1/ " FA-4	-0.70323
"	FA-2/ " FA-6	-0.80477 ----(Reject)
"	FA-2/ " FA-5	-0.73207
"	FA-3/ " FA-6	-0.866934----(Reject)

average $\alpha_{FeAl} = -0.714$

std. devn. $= \pm 0.015$

(c)

Solution	C_{Fe}	C_{Al}	C_M	(cps) $I^{My}_{FeK\alpha}$	(cps) $I^{Corr.\ by\ M}_{FeK\alpha}$	(cps) $I^{Corr.}_{FeK\alpha}$	(cps) $I^{o}_{FeK\alpha}$
FA-1	0.02000	0.00000	0.98000	31308	3679	3679	183950
FA-2	0.02000	0.01000	0.97000	30774	3893	3673	183650
FA-3	0.02000	0.01500	0.96500	30451	3990	3664	183200
FA-4	0.02000	0.02000	0.96000	30291	4105	3672	183600
FA-5	0.02000	0.02500	0.95500	30027	4204	3668	183400
FA-6	0.01828	0.02742	0.95420	27824	3916	3371	184409

average $I^{o}_{FeK\alpha}$ = 183700 cps.

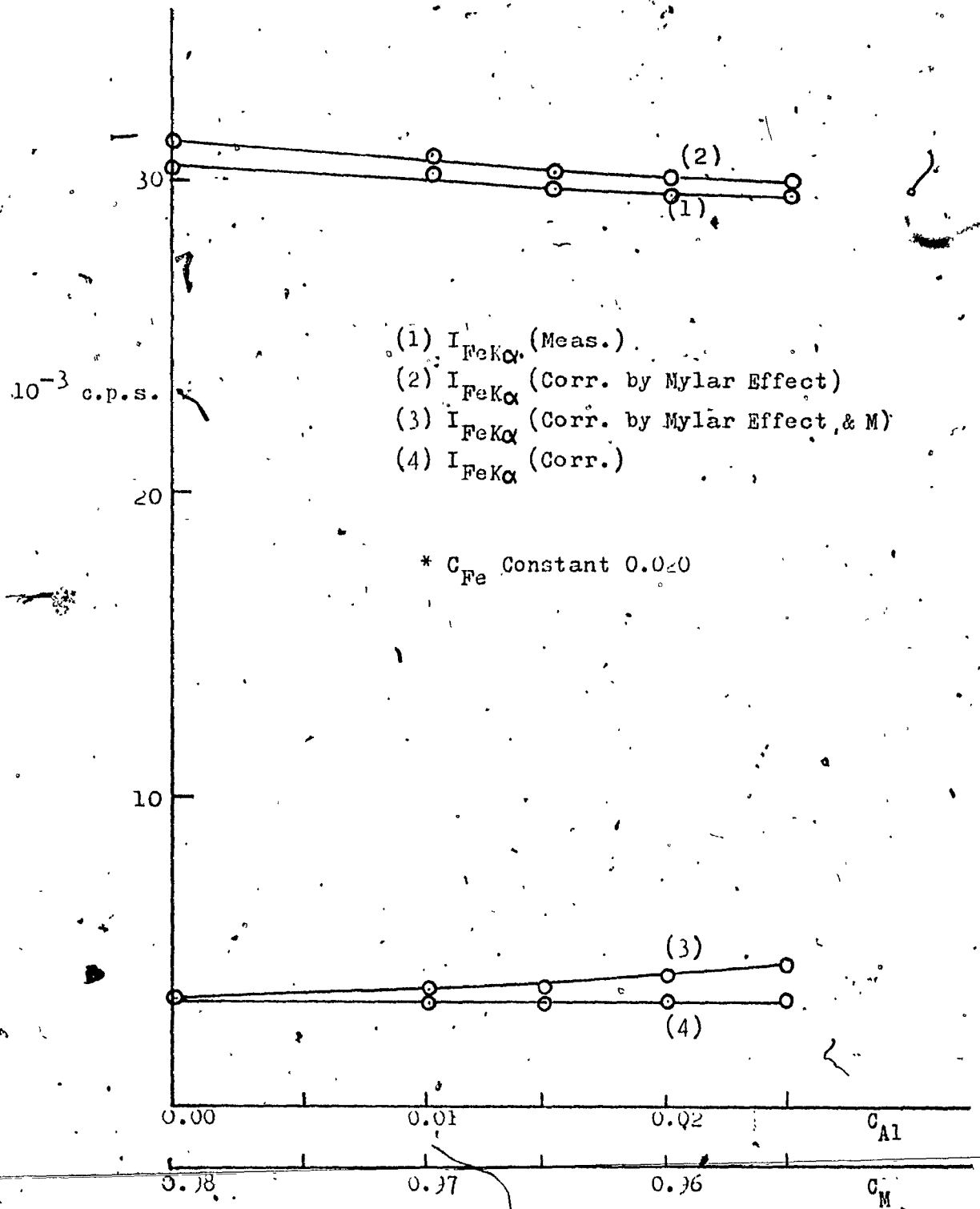
std. devn. = ± 400 cps

(d)

Solution	C_{Fe}	$I^{Corr}_{FeK\alpha}$ (cps)	$C^{Back\ cal.}_{Fe}$	Abs. error	% error
FA-1	0.02000	3679	0.02003	0.00003	0.15
FA-2	0.02000	3673	0.01999	0.00001	0.05
FA-3	0.02000	3664	0.01995	0.00005	0.25
FA-4	0.02000	3672	0.01999	0.00001	0.05
FA-5	0.020	3668	0.01997	0.00003	0.15
FA-6	0.01828	3371	0.01835	0.00007	0.38

FIGURE 4.2.4.2

$I_{FeK\alpha}$ VERSUS C_{Al} AND C_M



4.4.4.3 EFFECT OF Cl AND M

(a)

Solution	C_{Fe}	C_{Cl}	C_M	$I^{meas}_{FeK\alpha}$ (cps	$I^{My}_{FeK\alpha}$ (cps)
FCl-1	0.01000	0.00000	0.99000	16395	16700
FCl-2	0.01000	0.02158	0.96842	13743	13999
FCl-3	0.01000	0.04316	0.94684	11878	12099
FCl-4	0.01000	0.06474	0.92526	10387	10580
FCl-5	0.01000	0.08632	0.90368	9291	9464
FCl-6	0.01000	0.10790	0.88210	8359	8514

(b)

	α_{FeCl}
Solution FCl-1/Solution FCl-6	0.066321
" FCl-1/ " FCl-5	0.060541
" FCl-1/ " FCl-4	0.068944
" FCl-2/ " FCl-6	0.064726
" FCl-2/ " FCl-5	0.055239--(Reject)
" FCl-3/ " FCl-6	0.080594--(Reject)

average $\alpha_{FeCl} = 0.065^1$

std. devn. $= \pm 0.003^5$

(c)

Solution	C_{Fe}	C_{Cl}	C_M	$I^{My}_{FeK\alpha}$ (cps)	$I_{FeK\alpha}$ (cps) Corr. by M	$I_{FeK\alpha}$ (cps) Corr.	$I^{o}_{FeK\alpha}$ (cps)
FC1-1	0.01000	0.00000	0.99000	16700	1812	1812	181200
FC1-2	0.01000	0.02158	0.96842	13999	1791	1810	181000
FC1-3	0.01000	0.04316	0.94684	12099	1783	1817	181700
FC1-4	0.01000	0.06474	0.92526	10580	1765	1809	180900
FC1-5	0.01000	0.08632	0.9036	9464	1763	1816	181600
FC1-6	0.01000	0.10790	0.882	8514	1751	1811	181100

average $I^{o}_{FeK\alpha}$ = 181200 cps

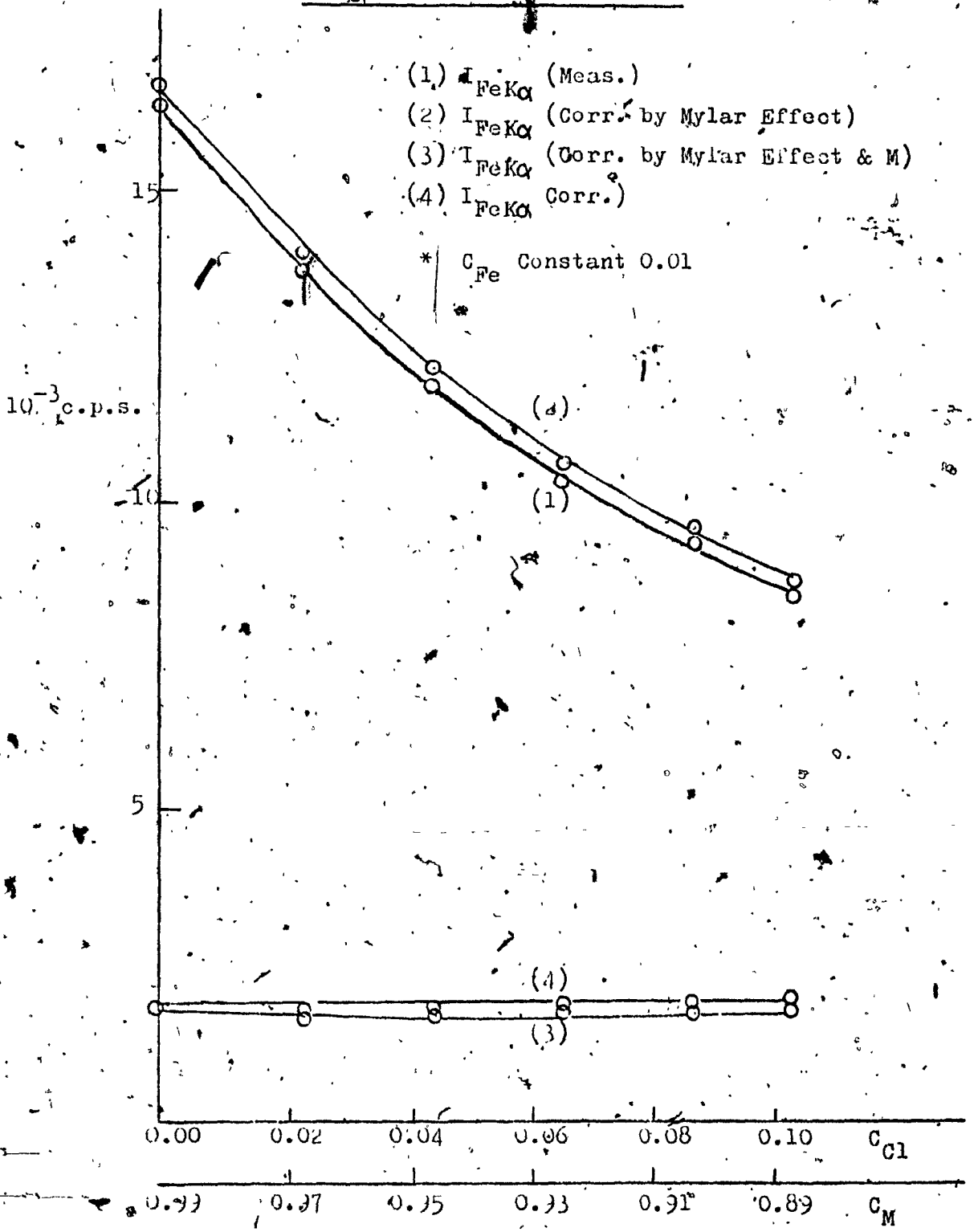
std. devn. = ± 400 cps

(d)

Solution	C_{Fe}	$I_{FeK\alpha}$ (cps) Corr.	C_{Fe} Back cal.	Abs. error	% error
FC1-1	0.01000	1812	0.01000	0.00000	0.00
FC1-2	0.01000	1810	0.00999	0.00001	0.10
FC1-3	0.01000	1817	0.01003	0.00003	0.30
FC1-4	0.01000	1809	0.00998	0.00002	0.20
FC1-5	0.01000	1816	0.01002	0.00002	0.20
FC1-6	0.01000	1811	0.00999	0.00001	0.10

FIGURE 4.2.4.3

$I_{FeK\alpha}$ VERSUS C_{Cl} AND C_M



4.2.5 EFFECT ON Ni

INSTRUMENT PARAMETERS

TUBE TARGET	W
kV	50
mA	20
COUNTER	Scin.
COLLIMATOR	Fine
CRYSTAL	LiF
HIGH VOLTAGE DETECTOR	3.50
GAIN	10
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	48.61
2θ Background	47.20
ω	0.08
COUNTING TIME	10 sec.

4.2.5.1 EFFECT OF M ON Ni

(a)

Solution	C_{Ni}	C_M	$I^{meas}_{NiK\alpha}$ (cps)	$I^{My}_{NiK\alpha}$ (cps)
N-1	0.01000	0.99000	44085	44526
N-2	0.02000	0.98000	80573	81370
N-3	0.03000	0.97000	110140	111241
N-4	0.05000	0.95000	158075	159656
N-5	0.08000	0.92000	207885	209964
N-6	0.10000	0.90000	233183	235515

(b)

	α_{NiM}
Solution N-1/Solution N-6	-0.91654
" N-1/ " N-5	-0.91701
" N-1/ " N-4	-0.91624
" N-2/ " N-6	-0.91748
" N-2/ " N-5	-0.91825
" N-3/ " N-6	-0.91587

average α_{NiM} = -0.916^9

std. devn. = $\pm 0.001^0$

(c)

Solution	C_{Ni}	C_M	(cps) $I^{My}_{NiK\alpha}$	(cps) $I^{Corr.\ by\ M'}_{NiK\alpha}$	(cps) $I^{o}_{NiK\alpha}$
N-1	0.01000	0.99000	44526	4108	410800
N-2	0.02000	0.98000	81379	8255	412750
N-3	0.03000	0.97000	111241	12304	410133
N-4	0.05000	0.95000	159656	20587	411740
N-5	0.08000	0.92000	209964	32849	408100
N-6	0.10000	0.90000	235515	41166	411660

average $I^{o}_{NiK\alpha}$ = 411000 cps

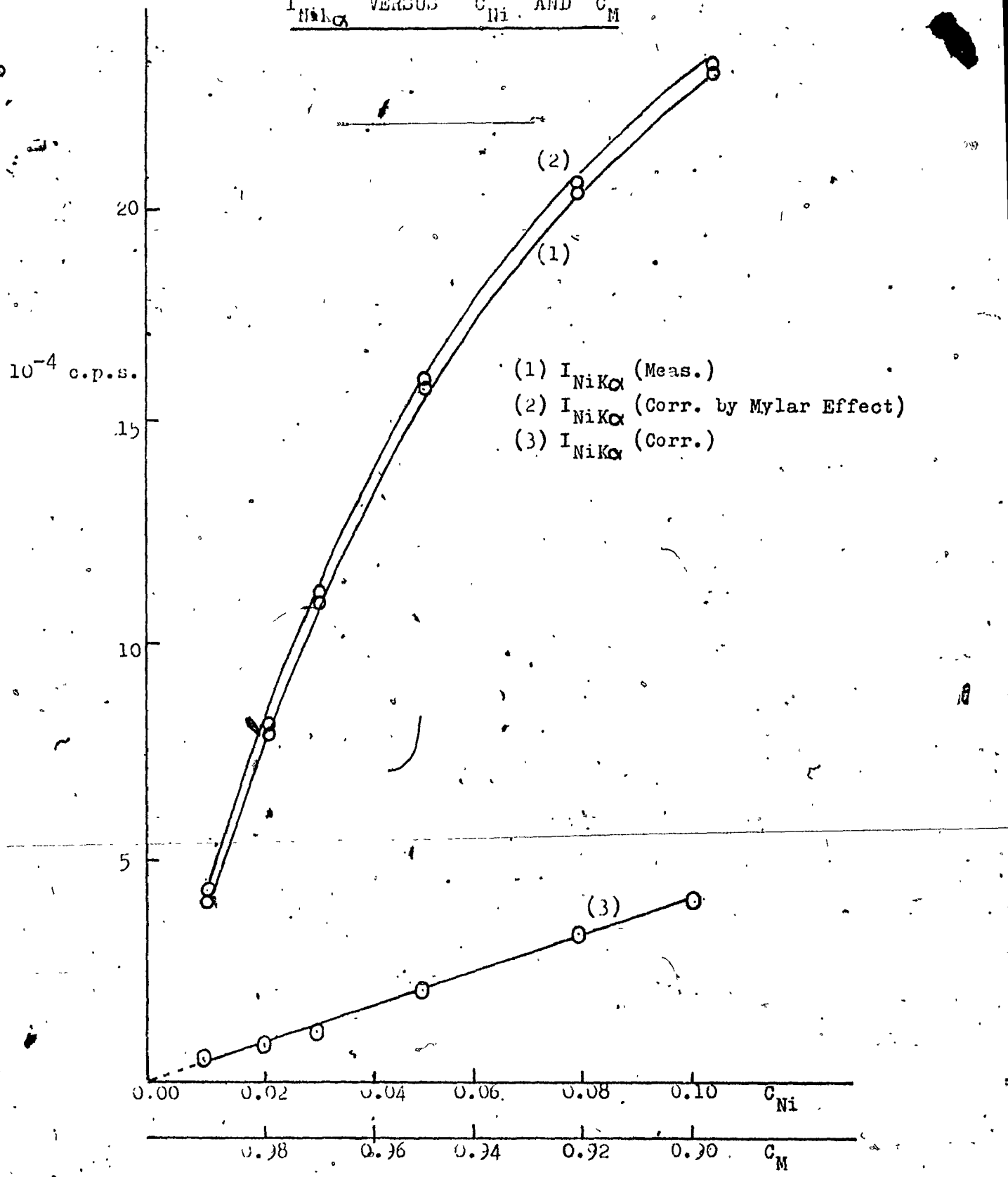
std. devn. = ± 1000 cps

(d)

Solution	C_{Ni}	(cps) $I^{Corr}_{NiK\alpha}$	$C^{Back\ cal.}_{Ni}$	Abs. error	% error
N-1	0.01000	4108	0.01000	0.00000	0.00
N-2	0.02000	8255	0.02009	0.00009	0.45
N-3	0.03000	12304	0.02994	0.00006	0.20
N-4	0.05000	20587	0.05010	0.00010	0.20
N-5	0.08000	32849	0.07994	0.0000	0.07
N-6	0.10000	41166	0.10018	0.00018	0.18

FIGURE 4.2.6.1

$I_{NiK\alpha}$ VERSUS C_{Ni} AND C_M



4.2.5.2 EFFECT OF Al AND M ON Ni

(a)

Solution	C_{Ni}	C_{Al}	C_M	$I^{meas}_{NiK\alpha}$ (cps)	$I^{My}_{NiK\alpha}$ (cps)
NA-1	0.02000	0.00000	0.98000	81257	82070
NA-2	0.02000	0.01000	0.97000	80332	81135
NA-3	0.02000	0.01500	0.96500	80020	80820
NA-4	0.02000	0.02000	0.96000	79664	80461
NA-5	0.02000	0.02500	0.95500	79019	79809
NA-6	0.01860	0.02791	0.95349	73862	74601

(b)

	α_{NiAl}
Solution NA-1/Solution NA-6	-0.78691
" NA-1/ " NA-5	-0.80195
" NA-1/ " NA-4	-0.81548
" NA-2/ " NA-6	-0.77947
" NA-2/ " NA-5	-0.80328
" NA-3/ " NA-6	-0.75692 - - - (Reject)

average α_{NiAl} = - 0.797

std. devn. = ± 0.014

(c)

Solution	C_{Ni}	C_{Al}	C_M	(cps) $I^{My}_{NiK\alpha}$	(cps) $I^{Corr.\ by\ M}_{NiK\alpha}$	(cps) $I^{Corr.}_{NiK\alpha}$	(cps) $I^{o}_{NiK\alpha}$
NA-1	0.02000	0.00000	0.98000	82070	8325	8325	416250
NA-2	0.02000	0.01000	0.97000	81135	8974	8327	416350
NA-3	0.02000	0.01500	0.96500	80820	9310	8344	417200
NA-4	0.02000	0.02000	0.96000	80461	9637	8354	417700
NA-5	0.02000	0.02500	0.95500	79809	9925	8335	416750
NA-6	0.01860	0.02791	0.95349	74601	9381	7722	415161

average $I^{o}_{NiK\alpha}$ = 416600 cps

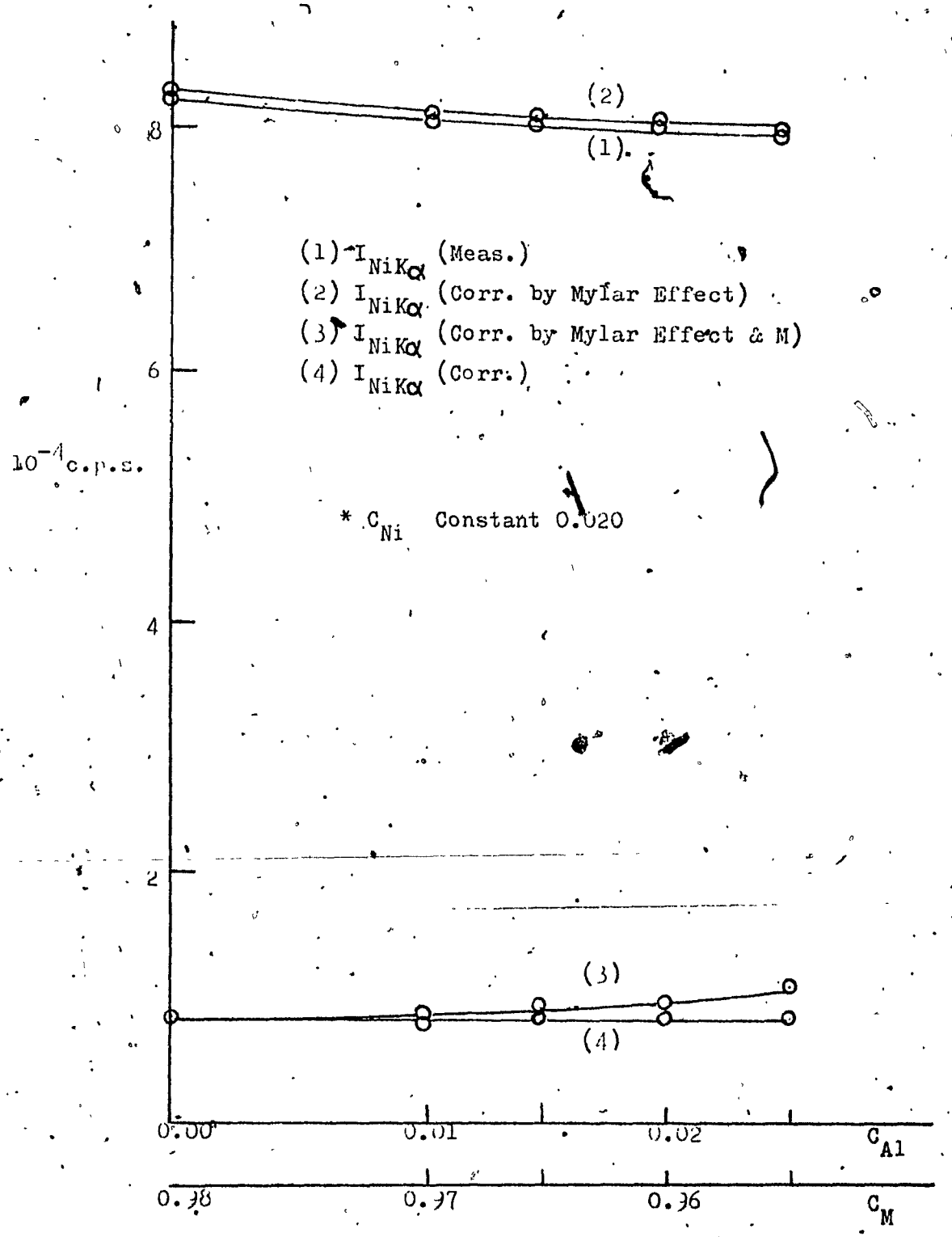
std. devn. = ± 1000 cps

(d)

Solution	C_{Ni}	$I^{Corr.}_{NiK\alpha}$ (cps)	$C^{Back\ cal.}_{Ni}$	Abs error	% error
NA-1	0.02000	8325	0.01998	0.00002	0.10
NA-2	0.02000	8327	0.01999	0.00001	0.05
NA-3	0.02000	8344	0.02003	0.00003	0.15
NA-4	0.02000	8354	0.02005	0.00005	0.25
NA-5	0.02000	8325	0.01998	0.00002	0.10
NA-6	0.01860	7722	0.01854	0.00006	0.34

FIGURE 4.1,5.2

I_{NiK_α} VERSUS C_{Al} AND C_M



4.2.5.3 EFFECT OF Cl AND M ON Ni

(a)

Solution	C_{Ni}	C_{Cl}	C_M	(cps) $I^{meas}_{NiK\alpha}$	(cps) $I^{My}_{NiK\alpha}$
NCl-1	0.01000	0.00000	0.99000	44017	44457
NCl-2	0.01000	0.02158	0.96842	37316	37689
NCl-3	0.01000	0.04316	0.94684	32455	32780
NCl-4	0.01000	0.06474	0.92526	28676	28963
NCl-5	0.01000	0.08632	0.90368	25672	25929
NCl-6	0.01000	0.10791	0.88209	23246	23478

(b)

		α_{NiCl}
Solution	NCl-1/Solution NCl-6	-0.15298
"	NCl-1/ " NCl-5	-0.15312
"	NCl-1/ " NCl-4	-0.15450
"	NCl-2/ " NCl-6	-0.15481
"	NCl-2/ " NCl-5	-0.15539
"	NCl-3/ " NCl-6	-0.14993

average α_{NiCl} = -0.153^5

std. devn. = $\pm 0.002^0$

(c)

Solution	C_{Ni}	C_{Cl}	C_M	(cps) $I^{My}_{NiK\alpha}$	(cps) $I^{Corr.\ by\ M}_{NiK\alpha}$	(cps) $I^{Corr.}_{NiK\alpha}$	(cps) $I^{o}_{NiK\alpha}$
NCl-1	0.01000	0.00000	0.99000	44457	4102	4102	410200
NCl-2	0.01000	0.02158	0.96842	37689	4223	4098	409800
NCl-3	0.01000	0.04316	0.94684	32780	4336	4118	411800
NCl-4	0.01000	0.06474	0.92526	28963	4392	4104	410400
NCl-5	0.01000	0.08632	0.90368	25929	4445	4101	410100
NCl-6	0.01000	0.10791	0.88209	23478	4489	4100	410000

average $I^{o}_{NiK\alpha}$ = 410400 cps

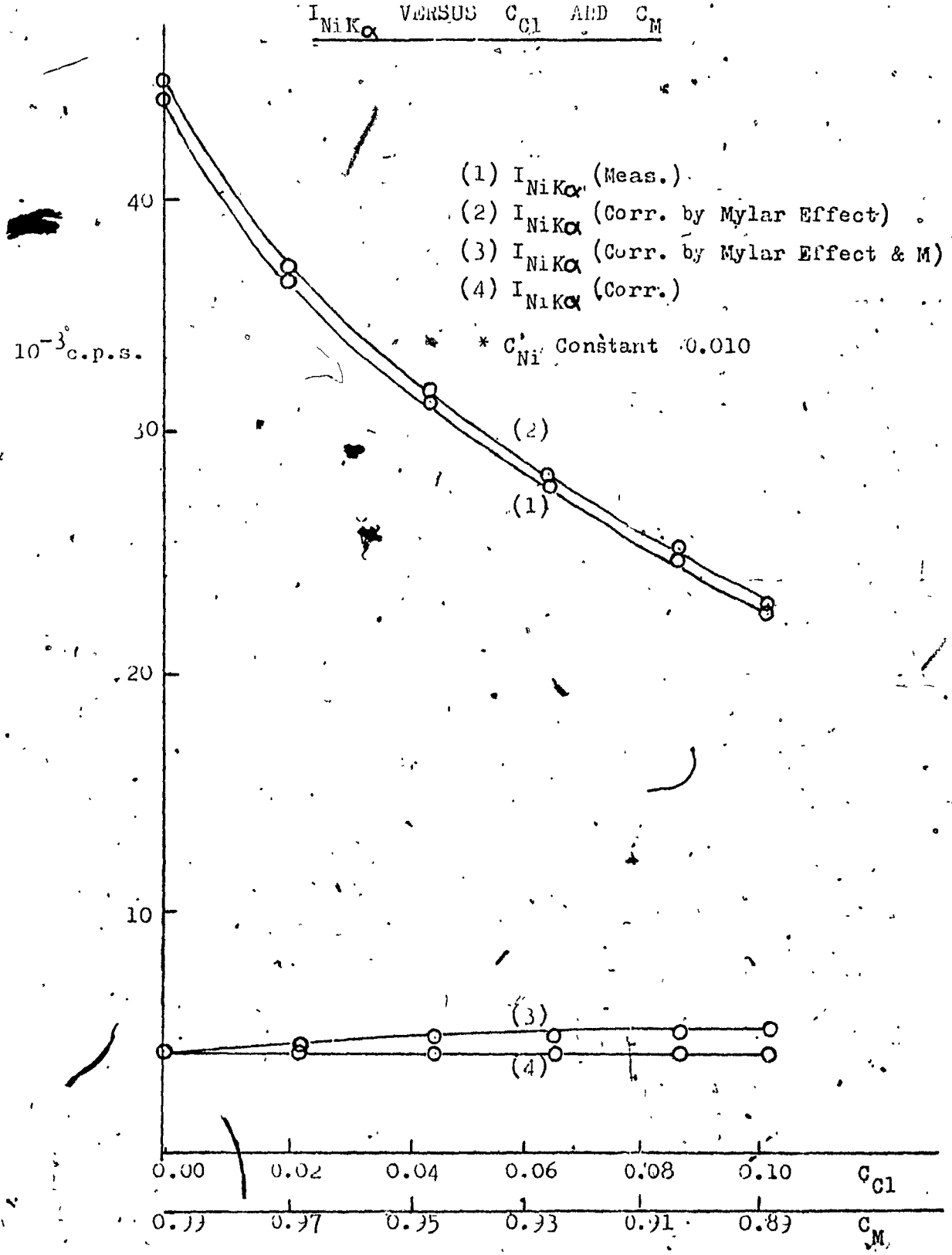
std. devn. = ± 700 cps

(d)

Solution	C_{Ni}	(cps) $I^{Corr.}_{NiK}$	$C^{Back\ cal.}_{Ni}$	Abs. error	% error
NCl-1	0.01000	4102	0.01000	0.00000	0.00
NCl-2	0.01000	4098	0.00999	0.00001	0.10
NCl-3	0.01000	4118	0.01003	0.00003	0.30
NCl-4	0.01000	4104	0.01000	0.00000	0.00
NCl-5	0.01000	4101	0.00999	0.00001	0.00
NCl-6	0.01000	4100	0.00999	0.00001	0.10

FIGURE 4.2.5.3

$I_{NiK\alpha}$ VERSUS C_{Cl} AND C_M



4.2.6 EFFECT ON Cu

INSTRUMENT PARAMETERS

TUBE TARGET	W
kV	50
mA	20
COUNTER	Scin.
COLLIMATOR	Fine
CRYSTAL	LiF
HIGH VOLTAGE DETECTOR	3.50
GAIN	10'
MODE	∞
UPPER LEVEL	0.00
LOWER LEVEL	0.30
ANGLES (degrees)	
2θ Peak	44.96
2θ Background	46.20
ω	0.00
COUNTING TIME	10 sec.

4.2.6.1 EFFECT OF M ON Cu

(a)

Solution	C_{Cu}	C_M	$I^{meas}_{CuK\alpha}$	$I^{MY}_{CuK\alpha}$
C-1	0.01000	0.99000	40982	41289
C-2	0.02000	0.98000	74188	74744
C-3	0.03000	0.97000	100723	101478
C-4	0.05000	0.95000	142048	143113
C-5	0.07000	0.93000	172554	173846
C-6	0.10000	0.90000	205400	206940

(b)

	α_{CuM}
Solution C-1/Solution C-6	-0.92556
" C-1/ " C-5	-0.92570
" C-1/ " C-4	-0.92540
" C-2/ " C-6	-0.92675
" C-2/ " C-5	-0.92480
" C-3/ " C-6	-0.92585

Average α_{CuM} = -0.925

std. devn. = $\pm$ 0.002

(c)

Solution	C_{Cu}	C_M	(cps) $I^{My}_{CuK\alpha}$	(cps) $I^{Corr.\ by\ M}_{CuK\alpha}$	(cps) $I^{o}_{CuK\alpha}$
C-1	0.01000	0.99000	41289	3450	345000
C-2	0.02000	0.98000	74744	6937	346850
C-3	0.03000	0.97000	101478	10358	345267
C-4	0.05000	0.95000	143113	17257	345140
C-5	0.07000	0.93000	173848	24182	345457
C-6	0.10000	0.90000	206940	34532	345320

average $I^{o}_{CuK\alpha}$ = 345500 cps

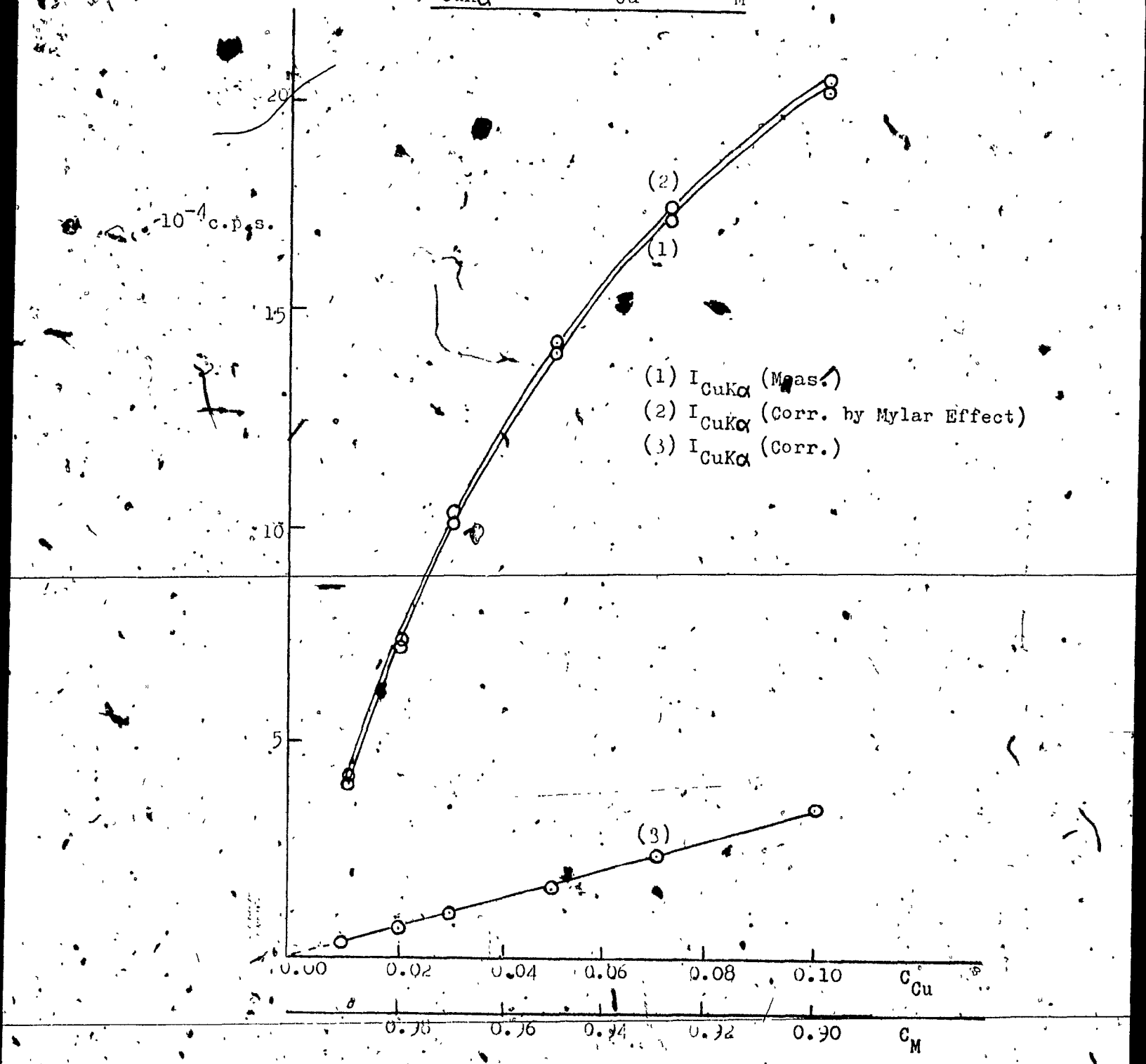
std. devn. = ± 400 cps

(d)

Solution	C_{Cu}	(cps) $I^{Corr.}_{CuK\alpha}$	$C^{Back\ cal.}_{Cu}$	Abs. error	% error
C-1	0.01000	3450	0.00999	0.00001	0.10
C-2	0.02000	6937	0.02008	-0.00008	0.04
C-3	0.03	10358	0.02998	0.00002	0.07
C-4	0.05	17257	0.04995	0.00005	0.10
C-5	0.07	24182	0.06999	0.00001	0.01
C-6	0.10	34532	0.09995	0.00005	0.05

FIGURE 4.6.1

$I_{CuK\alpha}$ VERSUS C_{Cu} AND C_M



4.2.6.2 EFFECT OF Al AND M ON Cu

(a)

Solution	C_{Cu}	C_{Al}	C_M	(cps) $I^{meas}_{CuK\alpha}$	(cps) $I^{My}_{CuK\alpha}$
CA-1	0.02000	0.00000	0.98000	72325	72867
CA-2	0.02000	0.01000	0.97000	72182	72723
CA-3	0.02000	0.01500	0.96500	71917	72459
CA-4	0.02000	0.02000	0.96000	71618	72155
CA-5	0.02000	0.02500	0.95500	71444	71980
CA-6	0.01872	0.02808	0.95320	67290	67795

(b)

		α_{CuAl}
Solution	CA-1/Solution CA-6	-0.86358
"	CA-1/ " CA-5	-0.87995
"	CA-1/ " CA-4	-0.87991
"	CA-2/ " CA-6	-0.83224
"	CA-2/ " CA-5	-0.86139
"	CA-3/ " CA-6	-0.83228

average α_{CuAl} = - 0.85

std. devn. = $\pm$ 0.02

(c)

Solution	C_{Cu}	C_{Al}	C_M	(cps) $I^{My}_{CuK\alpha}$	(cps) $I^{Corr.\ by\ M}_{CuK\alpha}$	(cps) $I^{Corr.}_{CuK\alpha}$	(cps) $I^{o}_{CuK\alpha}$
CA-1	0.02000	0.00000	0.98000	72867	6763	6763	338154
CA-2	0.02000	0.01000	0.97000	72723	7423	6798	339900
CA-3	0.02000	0.01500	0.96500	72459	7731	6797	339850
CA-4	0.02000	0.02000	0.96000	72155	8033	6793	339650
CA-5	0.02000	0.02500	0.95500	71980	8347	6801	340050
CA-6	0.01872	0.02808	0.95320	67795	7974	6339	338622

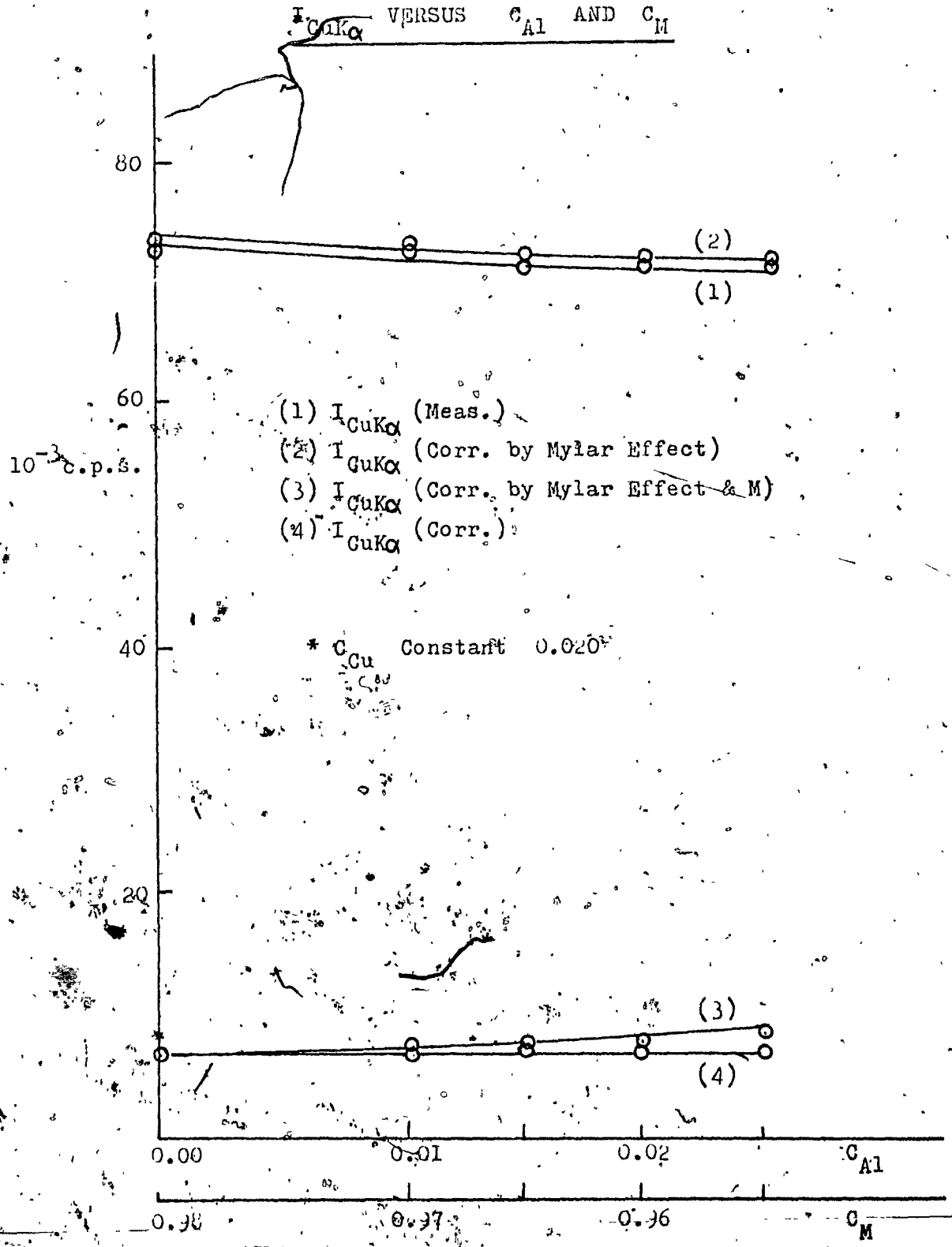
average $I^{o}_{CuK\alpha}$ = ~~339400~~ cps

std. devn. = $\pm$ 800 cps

(d)

Solution	C_{Cu}	(cps) $I^{Corr.}_{CuK\alpha}$	$C^{Back\ cal.}_{Cu}$	Abs. error	% error
CA-1	0.02000	6763	0.01993	0.00007	0.35
CA-2	0.02000	6798	0.02003	0.00003	0.15
CA-3	0.02000	6797	0.02003	0.00003	0.15
CA-4	0.020	6793	0.02001	0.00001	0.05
CA-5	0.020	6801	0.02003	0.00003	0.15
CA-6	0.01872	6339	0.01868	0.00004	0.24

FIGURE 4.2.6.2


$I_{CuK\alpha}$ VERSUS C_{Al} AND C_M
80
60
40
20
10^{-3} c.p.s.
(1) $I_{CuK\alpha}$ (Meas.)
(2) $I_{CuK\alpha}$ (Corr. by Mylar Effect)
(3) $I_{CuK\alpha}$ (Corr. by Mylar Effect & M)
(4) $I_{CuK\alpha}$ (Corr.)
* C_{Cu} Constant 0.020
(2)
(1)
(3)
(4)
0.00
0.01
0.02
C_{Al}
0.98
0.97
0.96
C_M

4.2.6.3 EFFECT OF Cl AND M ON Cu

(a)

Solution	C_{Cu}	C_{Cl}	C_M	$I^{meas}_{CuK\alpha}$	$I^{My}_{CuK\alpha}$
CCl-1	0.01000	0.00000	0.99000	40756	41062
CCl-2	0.01000	0.02158	0.96842	34692	34952
CCl-3	0.01000	0.04316	0.94684	30044	30269
CCl-4	0.01000	0.06473	0.92527	26629	26829
CCl-5	0.01000	0.08632	0.90368	23841	24020
CCl-6	0.01000	0.10791	0.88209	21577	21739

(b)

		α_{CuCl}
Solution	CCl-1/Solution CCl-6	-0.23740
"	CCl-1/ " CCl-5	-0.23895
"	CCl-1/ " CCl-4	-0.24103
"	CCl-2/ " CCl-6	-0.23196
"	CCl-2/ " CCl-5	-0.23328
"	CCl-3/ " CCl-6	-0.23924

average α_{CuCl} = -0.237

std. devn. = ±0.003

(c)

Solution	C_{Cu}	C_{Cl}	C_M	(cps) $I^{My}_{CuK\alpha}$	(cps) $I^{Corr.\ by\ M}_{CuK\alpha}$	(cps) $I^{Corr.}_{CuK\alpha}$	(cps) $I^{o}_{CuK\alpha}$
CCl-1	0.01000	0.00000	0.99000	41062	3431	3431	343100
CCl-2	0.01000	0.02158	0.96842	34952	3619	3440	344000
CCl-3	0.01000	0.04316	0.94684	30269	3739	3429	342900
CCl-4	0.01000	0.06473	0.92527	26829	3850	3438	343800
CCl-5	0.01000	0.08632	0.90368	24020	3926	3435	343500
CCl-6	0.01000	0.10791	0.88209	21739	3988	3432	343200

average $I^{o}_{CuK\alpha}$ = 343400 cps

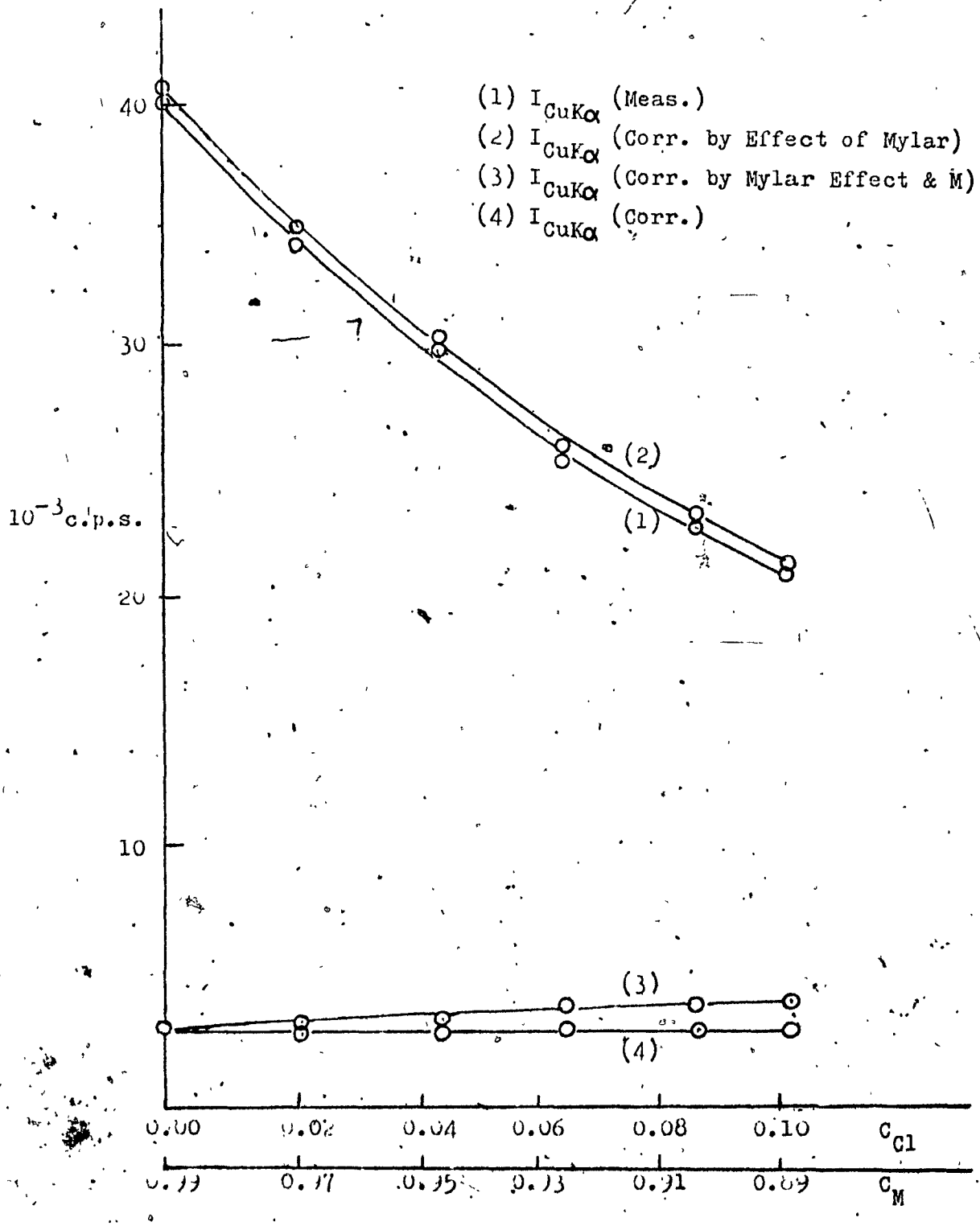
std. devn. = ± 400 cps

(d)

Solution	C_{Cu}	$I^{Corr.}_{CuK\alpha}$ (cps)	$C^{Back\ cal.}_{Cu}$	Abs. error	% error
CCl-1	0.01000	3431	0.00999	0.00001	0.10
CCl-2	0.01000	3440	0.01002	0.00002	0.20
CCl-3	0.01000	3429	0.00999	0.00001	0.10
CCl-4	0.01000	3438	0.01001	0.00001	0.10
CCl-5	0.01000	3435	0.01000	0.00000	0.00
CCl-6	0.01000	3432	0.00999	0.00001	0.10

FIGURE 4.2.6.3

$I_{CuK\alpha}$ VERSUS C_{Cl} AND C_M



REFERENCES

1. Claisse, F., Quebec Department of Mines, Progress Report 402, (1960)

2. Claisse, F., Can. Spectroscopy., 12, 20, (1967)

3. Jenkins, R., and J.L. De Vries, Practical X-ray Spectrometry, Philips Technical Library, Macmillan, 2nd edition, p116, (1970)

4. Gillam, E., and H.T. Heal, Brit. J. Appl. Phys., 3, 353, (1952)

5. Sherman, J., Spectrochim. Acta, 7, 283, (1955)

6. Muller, R., Spectrochim. Acta, 18, 123, (1962)

7. Shiraiwa, T., and N. Fujino, Jap. J Appl. Phy., 5, 886, (1966)

8. Criss, J.W., and L.S. Birks, Anal. Chem., 40, 1080, (1968)

9. Noakes, G.E., ASTM Spec. Tech. Pub., 157, 57, (1954)

10. Birks, L.S., X-ray Spectrochemical Analysis, Interscience, 1969, p86

11. Claisse, F., and M. Quintin, Can. Spectroscopy., 12, 129 (1967)

12. Beattie, H.J., and R.M. Brissey, Anal. Chem., 26, 980, (1954)

13. Lachance, G.R., and R.J. Traill, Can. Spect., 11, 43, (1966)

14. Waterbury, G.R., and E.A. Hakkila, Anal. Chem., 37, 1773, (1965)

15. Zimmerman, J.B., and J.C. Ingles, Extraction Metallurgy Division, Report EMA 72-14, Department of Mines; Canada, 1972

16. Kang, C.C., E.U. Keel and E. Solomon, Anal. Chem., 32, 321, (1960)

17. Dwiggins, C.W., Anal. Chem., 36, 1577, (1964)

18. Dick, J.G., and A.D. Nguyen, Candn. Jrl. Specty., 19, 5, (1974)

19. Beard, D.W., and E.M. Proctor, Advances in X-Ray Analysis, Vol. 10, Plenum Press, New York, 1966, p517

20. Birks, L.S., X-Ray Spectrochemical Analysis, Vol. II in Chemical Analysis, eds., P.J. Elving and I.M. Kolthoff, Interscience, 2nd. edition, 1969. p.36.

21. Buwalda, J., Philips Serving Science and Industry, 10, 22, (1964)

22. Ruark, A., and F.E. Brammer, Phys. Rev., 52, 322, (1937)

23. Dick, J.G., and A.D. Nguyen, Candn. Jrl. Specty., 19, 4, (1974)

24. Lachance, G.R., Can. Spec., 15, 64, (1970)

25. Tertian, R., X-Ray Spec., 2, 95, (1973)

APPENDIX I

In an effort to improve the accuracy of the Lachance-Traill correction coefficients, Claisse and Quintin[11] modified the L-T equation to take into consideration the polychromaticity of the primary radiation beam. By considering the total fluorescent intensity as the sum of the intensities for each wavelength, they obtained a summation for the L-T equation. Their general equation is similar to the L-T equation, except for the inclusion of higher-order terms. They also conducted experimental investigations aimed at proving the existence of these high-order terms, and estimating their magnitude in binary mixtures involving the oxides of iron, nickel and chromium. In this system, the single correction coefficient α_{AB} of the L-T system for a binary mixture is given by:-

$$\alpha_{AB} = \alpha_B + \alpha_{BB}C_B^2 + \alpha_{BBB}C_B^3 + \ldots + \alpha_{B\ldots nB}C_B^{(n-1)} \qquad (26)$$

They found that only the second-order term α_{BB} is significant, and that it is particularly significant where enhancement effects are involved. Therefore, the L-T equation may be rewritten as:-

$$C_A = R_A (1 + \alpha_B C_B + \alpha_{BB} C_B^2) \qquad (27)$$

In ternary system, an additional correction term has been proposed in order to take into account the effect of a third element on the second. This involves the product $C_B C_C$ in the Claisse and Quintin equation:-

$$C_A = R_A (1 + \alpha_B C_B + \alpha_C C_C + .. + \alpha_{BB} C_B^2 + \alpha_{CC} C_C^2 + .. + \alpha_{BC} C_B C_C + ...) \quad (28)$$

α_{BC}, on a theoretical basis,[24] can be calculated in all case, and that it is not constant. However, the results obtained by assuming α_{BC} constant show errors that are, in general, less significant than the precision and accuracy of the XRF and chemical analysis data.

APPENDIX II

Consider Equation (5) for a binary system:-

$$R_A = \frac{I_A}{I_A^o} = \frac{C_A}{1 + C_B(\bar{u}_B/\bar{u}_A - 1)} \qquad (29)$$

with $K_B = \bar{u}_B/\bar{u}_A$

Equation (29) can be rewritten as:-

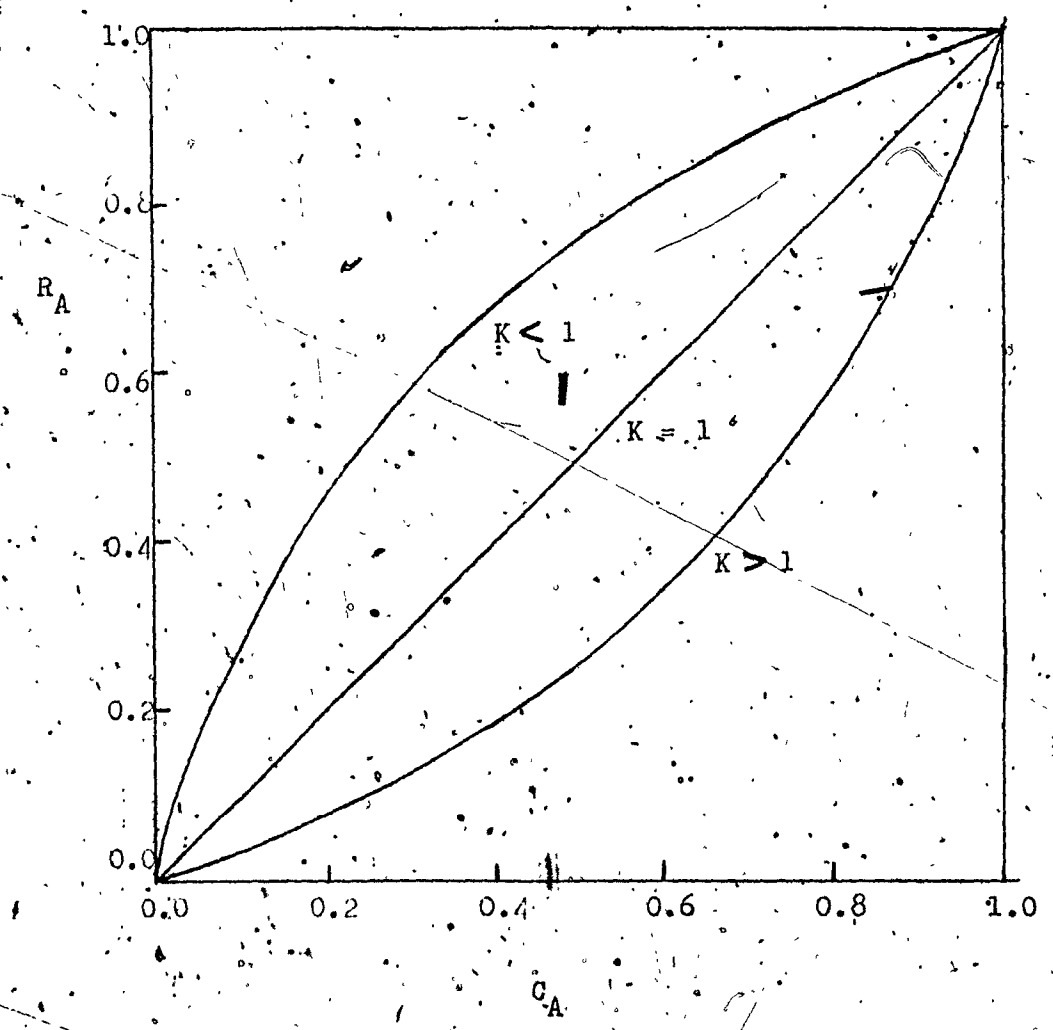
$$R_A = \frac{C_A}{1 + (K_B - 1)C_B} \qquad (30)$$

If K_B is large than unity the lower curve on Figure A is obtained, and we speak of a positive absorption effect of B on A, and if K_B is less than unity we get the upper curve and speak of a negative absorption effect. If K_B happens by chance to be equal to unity there is no absorption effect, and we have the middle curve.

Each particular value of K determines a certain curve which is an arc of a hyperbola. Conversely, it is sufficient to know of one point on the curve, (i.e. accurate values of C_A and the corresponding R_A), to calculate K by the simple formula:-

FIGURE A

INTENSITY RATIO R_A VERSUS C_A



$$K_{} = \frac{1 - R_A}{R_A} \cdot \frac{C_A}{1 - C_A} \qquad (31)$$

which is a most useful relation. For instance, if one of the curves is distorted for some reason, then the curve is no longer an hyperbola and its K is no longer a constant. However, Equation (31) enables us to calculate K for any point on the curve, and thus to characterize the distortion of the curve by the variation of K.

Tertian[25] has carried out some interelement coefficient applications to the analysis of metal alloys. The following figures show the results of his investigation.

FLUORESCENCE OF IRON IN THE Fe-Co, Fe-Cr AND Fe-Si SYSTEMS

VARIATION OF K VALUES VERSUS C_{Fe}